AWTR SUMMARY REPORT JAN. 1962 - JUNE 1964 999-WP-24

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ADSORPTION

FOAM SEPARATION

ELECTRODIALYSIS

REVERSE OSMOSIS

DISTILLATION

FREEZING

EUTECTIC FREEZING

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SOLVENT EXTRACTION

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Water Supply and Pollution Control

SUMMARY REPORT

JAN 1962–JUNE 1964

Advanced Waste Treatment Research

U. S. DEPARTMENT OF HEALTH
EDUCATION, AND WELFARE
Public Health Service

SUMMARY REPORT

THE
ADVANCED WASTE TREATMENT RESEARCH PROGRAM

January 1962 through June 1964

The Advanced Waste Treatment Research Program
Basic and Applied Sciences Branch
Robert A. Taft Sanitary Engineering Center

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Division of Water Supply and Pollution Control

April 1965

The ENVIRONMENTAL HEALTH SERIES of reports was established to report the results of scientific and engineering studies of man's environment: The community, whether urban, suburban, or rural, where he lives, works, and plays; the air, water, and earth he uses and reuses; and the wastes he produces and must dispose of in a way that preserves these natural resources. This SERIES of reports provides for professional users a central source of information on the intramural research activities of Divisions and Centers within the Public Health Service, and on their cooperative activities with State and local agencies, research institutions, and industrial organizations. The general subject area of each report is indicated by the two letters that appear in the publication number; the indicators are

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Public Health Service Publication No. 999-WP-24

FOREWORD

WHAT IS ADVANCED WASTE TREATMENT?

Water Use and Re-use

> "It now seems apparent that not only in Southern California but throughout the world, one-time use of water has become a luxury we can no longer afford. . . "
>
> John D. Parkhurst,
> Chief Engineer & General Manager
> Los Angeles County Sanitation Districts

Today, many communities draw their water supplies from watercourses that contain waste discharges from upstream locations; rare indeed is a community that enjoys water not previously used, at least in part, by a neighbor. With towns, irrigated agriculture, and industrial plants scattered across our watersheds, natural waterways are being used to carry increasing amounts of waste materials while simultaneously serving as the source of water supply for downstream users. If we consider usage for agricultural, recreational, and other miscellaneous purposes, we must accept the fact that nearly all surface and ground waters have had some previous use. Broadly interpreted then, all use is actually re-use. Thus, although the thought of deliberately re-using treated municipal waste waters may be a startling concept to the average citizen, this practice, to varying degrees, is already widespread and is gaining momentum as our burgeoning population demands more and more water for more and more uses.

A sign of our space age technology is the extent to which complex organic compounds, metallic salts, and other "exotic" chemicals are finding their way into our waste waters, our natural waterways, and eventually into our drinking water supplies. Moreover, today's conventional water and waste treatment processes are not capable of efficiently removing certain classes of contaminants from water. These resistant, or "refractory," materials range from simple inorganic salts through an ever-increasing number of highly complex, synthetic organic chemicals. Strong evidence exists that traces of directly identifiable synthetic organic chemicals can travel hundreds of miles downriver from their point of introduction, pass through the most modern water treatment plant, and be detected in measurable concentrations in tapwater. The sources of these byproducts of modern technology are not limited to industrial and commercial waste effluents but extend also into the American household where, for example, once-common biodegradable soaps have been replaced by synthetic detergents that are known to pass through the most modern sewage treatment plants with only partial removal. The detergent problem may, however, be largely solved within the next few years by the introduction of more readily biodegradable ("soft") detergents. Note, however, that "soft" detergents will not solve the refractory contaminant problem, for detergents constitute less than 10 percent of the total organic refractories in a typical municipal effluent.

The occurrence of these contaminating materials in domestic water supplies is becoming of increasing concern to municipal water supply authorities and also to public health officials. Since each cycle of use contributes its own refractory-contaminant increment, downstream users may encounter appreciable concentrations of these materials in untreated and even in treated water supplies. At present, the only practical solution for reducing the concentrations of certain contaminants is to dilute the polluted stream with a less contaminated water supply. This is the technique of "low-flow augmentation." It can, however, be a relatively expensive method of protecting water quality. Furthermore, in some locations, as the intensity of re-use inevitably increases, available dilution capacities will no longer suffice to maintain necessary water quality.

Urgently Needed: Complete Treatment Processes

> "Our luxury of relying on dilution by pristine waters and on purification by the great hydrologic cycle must inevitably end. We are approaching the time at which something better than present methods for treating waste waters must be used. . . . "
>
> David G. Stephan, Deputy Chief
> Advanced Waste Treatment Research Program
> Public Health Service

Many new physical-chemical separation processes are emerging as candidates for major roles in the waste treatment technology of the future. For the first time, the aim exists of returning used water to a purity at least as high as the original water supply before use. With the introduction of these processes will come a giant step forward in our fight to prevent pollution.

Obviously, as these "advanced waste treatment" processes are developed and brought into use, higher and higher effluent quality will be achieved. As this quality increases, the effluent itself will become of more and more value. At some point, depending on the total water resource picture at the location involved, the effluent water may become, literally, "too good to throw away." Deliberate re-use for agricultural, industrial, recreational, or even municipal purposes will be chosen. At this point, water renovation will have been accomplished; the treatment of waste water and the simultaneous provision of water supply will have been achieved.

The water needs of our nation are expanding rapidly in the face of diminishing or, at best, a constant supply. In recent years the urgency of this need in our arid areas has focused attention on the potential of municipal waste waters as an undeveloped source of usable water. Use of this potential resource appears to offer a promising solution to supplementing the water supply needs of many communities throughout the United States and the world. Water-short regions will normally be the first to face the prospect of deliberate waste-water renovation and re-use, but within the foreseeable future, the need to treat our waste waters more completely, both to abate pollution and allow repeated re-use, will become apparent even in the humid, water-rich parts of our country. Pollution control in these areas is, of course, a need more readily apparent to the layman, but the need for augmented water supplies in the future, and even in the present in some areas, is now demanding attention. In the arid and semiarid regions of our country and the world, the converse is generally true. The layman recognizes the great, sometimes urgent need for additional water supplies but is unaware of the effect of pollution on the total water resources of the region. Clearly, the problems are interrelated. Furthermore, the same solution—a practical water renovation technology—can help alleviate both problems.

The importance of developing new water supplies in arid regions is dramatized by a prediction in the recently released Pacific Southwest Water Plan prepared by the United States Department of Interior. This report estimates a water deficit of 5 million acre-feet in the Pacific Southwest (primarily southern California and Arizona) in the year 2000. It further states that possibly 2.7 million acre-feet of this deficit could be made up from "urban return flows through treatment of sewage water for re-use."

Unfortunately, practical and economical water renovation techniques do not exist beyond the laboratory scale. They must be further developed to meet the needs of the future if chemical, biological, and radiological pollutants are to be denied access to our waterways, and if taste- and odor-bearing materials and potentially toxic substances are to be eliminated from our tapwaters. Complete water renovation is already technically possible but at unreasonably high cost. The challenge is, therefore, to develop and refine existing technological principles to provide an economic solution; to accomplish this will require a concentrated program of research and development.

The degree of purification required for a given waste stream will be dictated by the specific re-use intended. Re-use for irrigation might require no or only slight inorganic removal and disinfection; re-use for industrial purposes might require elimination of foam producers, selective removal of corrosive or scale-forming inorganic components, and some reduction in gross organic load; re-use for recreational purposes might be accomplished with disinfection, removal of color-producing agents and suspended solids, and reduction of algal nutrients; re-use for municipal water supplies, on the other hand, would require complete removal of all suspended materials and organic impurities, reduction of inorganic salts to optimum levels, and positive disinfection with respect to microbiological components.

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PROGRAM SUMMARY

Separation of both organic and inorganic contaminants, though not a simple undertaking, can be accomplished to any degree desired, but considerable research and development are required to develop potential separation processes to the point of technical and economic practicability for large-scale operations. The Advanced Waste Treatment Research (hereafter referred to as AWTR) Program of the Public Health Service has begun and is continuing work in this direction; practical solutions appear near, but much remains to be done, and the effort must be accelerated.

This report brings up to date the findings of studies supported and conducted by the AWTR Program from January 1962 through June 1964. A previous report (AWTR-1) summarized activities of the AWTR Program from June 1960 through December 1961. Interim detailed project reports have also been issued (see Appendix D for listing).

LAW AUTHORIZING FEDERAL GOVERNMENT RESEARCH

To guarantee the availability of practical answers to the Nation's water resource needs, the Congress has enacted legislation directing research toward the development of better waste treatment processes. The Public Health Service's Division of Water Supply and Pollution Control established its AWTR Program at the Robert A. Taft Sanitary Engineering Center to meet this need. Specifically, with the passage of Public Law 87-88, in July 1961, amending the Federal Water Pollution Control Act, Congress directed the Secretary of Health, Education, and Welfare

> ". . . to develop and demonstrate practicable means of treating municipal sewage and other water-borne wastes to remove the maximum possible amounts of physical, chemical, and biological pollutants in order to restore and maintain the maximum amount of the Nation's water at a quality suitable for repeated reuse."

Under this authorization, the Public Health Service (PHS), through its AWTR Program and other activities, continues to spearhead the Federal Government's research efforts in this area.

PHS APPROACH TO THE PROBLEM

In contrast to sedimentation techniques and biological oxidation, which represent the basic concepts of conventional waste treatment processes, the AWTR Program is investigating a variety of physical-chemical separation processes that have the ability to remove dissolved salts and complex synthetic organic wastes unaffected by standard treatment. Broadly speaking, this Program is attempting to adapt both conventional and newly emerging chemical engineering separation processes to the solution of large-scale water purification problems. Processes studied to date include: adsorption, electrodialysis, foaming, distillation, solvent extraction, emulsion separation, freezing, hydration, chemical oxidation, ion exchange, electrochemical degradation, and reverse osmosis.

The bulk of research undertaken has been carried out through a series of negotiated contracts with universities, industries, and private research organizations. More recently, as the preliminary investigations have uncovered leads to promising methods of separation, increased effort has been spent in pursuing and developing these leads by direct research in the Public Health Service's Robert A. Taft Sanitary Engineering Center in Cincinnati, Ohio.

LEVEL OF FUNDS INVOLVED

Funds expended under the AWTR Program have ranged from $200,000 in Fiscal Year 1961 to $750,000 in Fiscal Year 1963, with contract research accounting for about 70 percent of the total research expenditures.

Over the Program's 3-1/2 years, individual research project expenditures assigned to outside contractors have ranged from as little as $500 up to $63,500. There were 16, 17, 26, and 19 individual contracts negotiated during the fiscal years 1961 through 1964, respectively.

REVIEW OF MAJOR ACCOMPLISHMENTS

Studies conducted under the AWTR Program have provided a sound basis for screening the several physical-chemical separation processes previously mentioned either into or out of a program of accelerated investigation and development. Four under investigation are currently considered as having unusually good prospects for being developed for large-scale use in improving the quality of conventionally treated waste waters. These early indications are particularly encouraging since the projected treatment costs on a scale-up basis are not greatly out of line with current costs associated with municipal use of water.

Adsorption by activated carbon for removal of organic compounds has been shown highly effective. Regeneration of the carbon has been proven possible. Despite the relatively high cost of activated carbon, the current outlook indicates that with a feed free of suspended solids, satisfactory results are attainable for a cost under 10 cents per 1,000 gallons of product water at the 10 million gallon per day (mgd) scale. At present, a 290,000-gallon-per-day (gpd) pilot plant is being designed and constructed.

Foam separation is a process that takes advantage of the foaming properties of a waste stream by passing air bubbles through the stream and causing surface-active organic impurities to concentrate at the bubble surfaces. A 500,000-gpd pilot unit has been operated for over 6 months. The process looks very promising as a method of removing up to 30 to 40 percent of the organic contaminants from a conventionally treated waste effluent. It also removes 70 to 80 percent of the synthetic detergent present. Costs should be less than 3 to 5 cents per 1,000 gallons at the 10-mgd scale and exclusive of foamate disposal.

Electrodialysis is a process for separating ionized materials from water by use of cation- and anion-permeable membranes placed in alternate sequence between two electrodes. Although not practical for removing organic molecules, it is highly effective in removing dissolved inorganic salts and would work well as part of a two-stage, organic-inorganic separation system. Exclusive of brine disposal, this process is expected to cost about 15 to 20 cents per 1,000 gallons of product water in a 10-mgd plant. The outlook is sufficiently promising to justify a pilot plant study, and plans are under way for an experimental unit handling 80,000 gpd feedwater.

Distillation, while particularly suited to feeds containing only nonvolatile contaminants, is expected to be adaptable to municipal waste waters containing certain volatile contaminants that may be carried over into the product. Although this situation constitutes a significant drawback to this process, the possibility of using followup polishing treatments to remove trace impurities offers a practical solution. Costs for treatment by distillation are still uncertain but probably will be something less than $1 per 1,000 gallons at a 10-mgd capacity. Even though this is a much higher unit cost than those for other processes under consideration, application of a "blending principle" can lead to very sizable savings (perhaps 50% or more) when a "total removal" process such as distillation is employed in the proper system configuration.

DISPOSAL OF CONCENTRATED IMPURITIES

An inescapable byproduct of any separation process is the concentrated waste produced. Final disposition of these wastes must be made without polluting either surface or underground water supplies. Since this ultimate disposal is a major consideration in the overall development of advanced waste treatment systems, disposal methods are being studied along with treatment processes. Possible solutions considered to date include: subsurface disposal into permeable strata or cavities; wet oxidation; incineration; conveyance to selected dump sites (e.g., the sea) by barge, truck, or pipeline; and recovery of waste materials to make useful products.

FUTURE COURSE OF AWTR

Research and development effort is being concentrated on processes that show promise of having reasonably good potential for success when applied either singly or in combination. Less promising separation processes will, however, be re-evaluated from time to time, and new techniques and approaches will be thoroughly investigated when they appear, because of the importance of achieving the best possible solutions to specific problems at the minimum possible costs.

FIELD EVALUATION PLANTS

Of great importance in developing advanced waste treatment (hereafter referred to as AWT) techniques into practical and workable solutions will be the conducting of detailed studies in full-scale field evaluation plants. Only by this means can practical answers be given to the many problems not ordinarily encountered in small-scale pilot operations, for example, the multiple complications associated with the day-to-day variations in composition of the waste stream. Beyond this, the suitability of the various processes and their component operations must be studied over extended periods to permit thorough understanding and solution of problems involving corrosion, scaling, materials of construction, membrane clogging, and so forth. Many other related aspects must undergo thorough testing under actual operating conditions before final recommendations can be made for widespread application of these processes.

ABSTRACT

This report summarizes activities of the Public Health Service's Advanced Waste Treatment Research Program from January 1962 through June 1964. Under an extensive contract research program, a wide range of physical-chemical separation processes have been studied to evaluate their effectiveness in purifying municipal and industrial waste waters. Laboratory investigations have shown that adsorption by granular activated carbon is an effective method of removing organic contaminants but that other materials studied as possible low-cost adsorbents failed to produce consistently effective organic removals. Laboratory and pilot plant foaming of secondary effluent removed 30 to 40 percent of the organic contaminants and 70 to 80 percent of synthetic detergents. Single-pass electrodialysis reduced the concentration of salts by 40 to 50 percent. Electrodialysis has shown sufficient promise in laboratory model stacks to merit installation of a 70,000-gpd pilot plant. Initial work on distillation has established that volatile contaminants carry over into the distillate to produce a detectable odor, requiring further treatment by activated carbon. Laboratory experiments on reverse osmosis indicate considerable promise for this process, but much development work remains to be done on factors such as membrane life, flux rates, and biological effects on membranes.

In studies on freezing, fine ice crystals are seen to agglomerate into large or massive chunks if the ice matrix is subjected to moderate compression. The agglomeration limits the ability to wash contaminants from the ice crystals. Solvent extraction, with low-molecular-weight secondary and tertiary amines, has produced water with an organic content of less than 10 milligrams per liter and a total dissolved solids content of less than 150 milligrams per liter. In anticipating various approaches to the chemical oxidation of organic contaminants in waste water, the active-oxygen process appears to offer the best potential for technical and economic success. Ultimate disposal of concentrated wastes resulting from the application of physical-chemical separation processes to waste waters has been considered by methods such as (1) wet oxidation, (2) incineration, (3) injection to porous underground formations, (4) placement in natural or man-made underground cavities (salt cavities, mined or nuclear blast cavities), and (5) disposal in the ocean after pipeline conveyance from point of origin.

SUMMARY REPORT ADVANCED WASTE TREATMENT RESEARCH PROGRAM

January 1962 through June 1964

Introduction

In carrying out the responsibility of Public Law 87-88, the AWTR Program has placed primary, but not exclusive, emphasis on the study of physical-chemical separation processes. Biological treatment methods have been and are being considered also, but most of the effort to date has been spent on nonbiological treatment because (1) biotreatments are less likely to be capable of the ultrahigh efficiency and inorganic removals required, and (2) major emphasis is already being given to biological treatment research by many other investigators both within and without the PHS. The Program has also sought to take full advantage of the Public Health Service's traditional and extensive background, experience, and competence in water supply and water pollution matters.

OBJECTIVES OF THE AWTR PROGRAM

Development of New Treatment Technology

The immediate objective of the Public Health Service's AWTR Program is to develop the needed new waste treatment technology to achieve a highly efficient, yet economical, separation of contaminants from their conveying waters. The Program plans to investigate every potential solution to establish the most effective removal process for each category of pollutants. In pursuing this objective, biological treatment and physical-chemical separation processes are being thoroughly studied, developed, and evaluated both separately and as combination processes, with technical and economic considerations serving as criteria for acceptability.

The problem of removing refractory contaminants from waste streams is alternately complicated by the relatively small concentrations of particularly objectionable materials, by the extreme range of conditions encountered in the types and amounts of pollutants present in a given stream, and by the variation in types of pollutants occurring from stream to stream. In one case, the item of concern may be excessive concentrations of total dissolved solids or of algal nutrients, whereas in another stream it may be only minute concentrations of an organic material. Needed then are methods of reducing the concentration of organic contaminants to a near-zero level and methods of controlling inorganic salts within a range of concentrations. Generally, methods that will remove a broad range of classes of materials will serve best, but special removal methods will also find wide use. If nitrates, phosphates, and ammonia could be selectively removed, advantages in treating for re-use would accrue. In many cases a system of two or more separation processes may be required to accomplish the desired degree of treatment.

The specific re-use to be made of a renovated waste water will establish the extent of contaminant removal required, this being another factor necessitating the development of several distinctively selective separation techniques.

Disposal of Contaminants

The desirability of simultaneous study of "separation" and "permanent disposal" processes is apparent from the fact that they are closely related both technically and economically. This relationship is best illustrated by noting that the continued concentration of a waste stream will produce an increasing quantity of product water and decreasing quantity of concentrated waste. Generally, however, the further the concentration step is carried, the higher the cost for concentration but the lower the cost for disposal of the reduced volume of waste.

ECONOMICS OF COMPLETE WATER RENOVATION

The technological adequacy of a separation process or an ultimate disposal process becomes the overriding criterion for determining the practicability of any given approach to the advanced treatment of municipal waste streams. Of major importance, however, is the matter of economics; a number of processes are technically capable of achieving the desired ends but only at an unreasonably high cost. Hence, the final measure of success for a particular process will be the cost, not only of the individual separation techniques, but of the complete treatment and disposal operation.

Basis of Cost Comparisons

Establishing a basis of comparison for evaluating the economic feasibility of an AWT technology obviously requires cost data. In this instance, however, the obtaining of exact cost data suitable to straightforward comparisons is impossible, partly because directly comparable cost data do not exist, and partly because many of the advantages inherent in the AWT concept have intangible values. For example, what dollar value can be assigned to a treatment process that eliminates an objectionable pollution problem from a stream or impoundment where pollution has not previously been eliminated? Or what is the worth of a supplementary clean water supply to be used for recreational purposes where such a supply has not been previously available? More to the point, how much is it worth to ascertain that chemical, biological, or radiological pollutants are not exerting subtle, cumulative effects on the health of man?

If we overlook, momentarily, the intangible values involved, and consider advanced waste treatment as simply another method of producing a usable supply of water, for whatever purpose, it is logical to compare the cost of this method of water production against the costs of conventional water treatment or sewage treatment, or both, that the advanced method could conceivably replace. Although existing cost data for conventional treatment processes may not be completely precise or representative, the best available average figures provide, at least, order-of-magnitude values to serve as a preliminary baseline on which comparisons can be made.

Using cost data reported in several independently conducted national surveys, McCallum[1] has analyzed and reported the water supply and waste treatment costs that can be ascribed to the major elements of the typical municipal water use cycle including (1) source development and transmission, (2) water treatment, (3) water distribution, (4) waste collection, and (5) waste treatment and disposal. Since advanced waste treatment could accomplish the first, second, and fifth functions, the sum of these costs in today's technology can reasonably be used as a baseline to estimate the competitive position of advanced waste treatment. The total cost of these functions amounts to about 23 cents per 1, 000 gallons on a national average and nearly 30 cents per 1, 000 gallons in prevailing high-cost areas of the country, areas that presumably will require advanced waste treatment at the earliest dates. A technology using new and more complex processes is not expected to compete on an equal basis costwise with present treatment technology. The "law of diminishing returns" dictates, however, that tomorrow's water will cost more and more even if today's techniques are continued, and the proposed new technology will provide a more nearly complete and more selective treatment than is achieved by today's less efficient techniques.

The foregoing figures are not, however, considered as definite cost goals that can hopefully be duplicated by an AWT technology; rather, they are intended only to give us some perspective with regard to present costs for fairly complete water and waste treatment operations. One important aspect of the AWTR study involves keeping an up-to-date interpretation of indicated treatment costs for each process under study. In this way, the cost advantage attributable to each new technological development can be evaluated and used to guide the course of future research in the most promising economic direction.

Since water tends to be valued by its production cost instead of its economic worth, the intent of the AWTR Program is to develop the technology that will achieve the desired pollution control and provide re-usable water at the very lowest possible cost. For every plant designed, a unique economic situation is expected to determine the optimum separation process, the optimum disposal technique, and the optimum fraction of the total treatment job each will be required to do. The final cost of a given renovated water will have to be based on all the treatment and handling steps involved, and not just on the "advanced" processes included. The expense incurred in disposing the final concentrated waste will be a part of this total cost.

Not all advanced treatment processes are necessarily aimed at complete removal of all materials from water. Suitable quality goals must be established for each type of water use, even for discharge to a receiving stream. Advanced treatment processes must meet these goals, and the more stringent the quality requirement, the higher the cost. Even for municipal purposes, official drinking water standards establish permissible levels of many natural ingredients in water supplies and further stipulate maximum acceptable limits for many specific compounds.

AWTR APPROACH TO PROCESS DEVELOPMENT

In the AWTR Program's plan of action, each potential waste treatment process progresses through a five-stage development program designed to give it full consideration and yet eliminate it if it proves impractical or unfeasible at any of the stages for either technical or economic reasons. The five stages are: (1) preliminary exploration, (2) feasibility research, (3) engineering development, (4) process evaluation, and (5) large-scale field evaluation.

Stage 1. Preliminary Exploration

Ideas are given a preliminary desktop evaluation and, where appropriate, are further evaluated through key experiments. Judgments about possible ultimate technical and economic practicability are made, recommendations for immediate future work (if any) are prepared, and relative priorities for additional evaluation and research are assigned.

Stage 2. Feasibility Research

Estimates of the probable technical and economic feasibility of candidate processes for use in water renovation are developed through formal research projects. The principal intent of the feasibility research studies is to screen various processes either out of current consideration or into immediate and intensive development by the Program.

Stage 3. Engineering Development

Engineering data and correlations are developed, operating and design variables are determined and roughly optimized, and broad-scale applicability is checked for processes that have passed the feasibility screen. The primary objective of the engineering development work is to predict, with a relatively high degree of confidence, the probable practical feasibility of the proposed processes.

Stage 4. Process Evaluation

Selected processes are evaluated and optimized on a realistic scale and under actual operating conditions to provide firm bases for establishing cost and performance data and develop design and operating correlations sufficiently complete that full-scale evaluation of the process under any reasonable conditions of feed composition, operating environment, and product quality requirements is possible.

Stage 5. Large-Scale Field Evaluation

Processes that have progressed through the previous four stages and appear worthy of complete development are tested in large-scale field evaluation plants. This final step is essential to establish the reliability, and the engineering, operating, and economic potential of the most promising treatment processes under conditions of daily and seasonal variations that occur in municipal waste streams. These plants are also needed to allow optimization of each of the integrated unit operations required for a given AWT system.

CONTRACT RESEARCH APPROACH

In contrast to most other research programs carried on at the Robert A. Taft Sanitary Engineering Center, this Program has been conducted principally through a series of negotiated contracts with universities, private research institutes, and industrial concerns. This departure from precedent permitted rapid entry into study areas requiring equipment and competencies available only in highly specialized research groups. Under this arrangement it has been possible to take the fullest advantage of a considerable amount of previous investigation and development, yet at the same time, to evaluate results in the light of PHS experience with conventional water and waste treatment results. Carried on concurrently with the outside research contract activities has been a steadily expanding program of complementary direct research in PHS laboratories. This combined in-house and extramural approach has proved of great value in attaining maximum research efficiency.

As a result of its past experience in water treatment and water pollution matters, the PHS is uniquely qualified to direct a program for developing advanced methods of renovating waste waters. For many years the PHS has been deeply involved in extensive surveys, studies, and investigations relating to the analysis, composition, and treatment of water supplies, municipal and industrial wastes, and polluted streams. This background of experience and competence has extended to all phases of water and stream pollution, ranging from conventional methods of treatment to the health effects of biological, radiological, and chemical pollutants. The extent to which natural stream purification is effective in reducing pollution, and the effect of both general and specific pollutants on the flora and fauna of the Nation's streams have also been measured and significant relationships developed. The broad experience and competencies gained over the years, are available, when needed, to help guide the AWT research, an advantage of particular value in such matters as establishing the level of pollutant removal required from a given process, or in providing knowledgeable guidance for developing relationships between conventional and advanced waste treatment processes.

CONTRACT RESEARCH ACTIVITIES

Principal investigations undertaken through outside research groups to date have involved adsorption, foaming, electrodialysis, reverse osmosis, solvent extraction, and freezing. Each research contract is monitored closely by a staff member of the AWTR Program specializing in the particular area of interest. Having the AWTR representative work closely with the contractor's research team permits the best possible coordination of the many different separation techniques under investigation and offers other advantages as well. PHS staff members, for example, develop specialized competencies through first-hand contact with each project. Furthermore, a change of direction or emphasis in a given approach can be authorized during the term of the contract if intermediate findings indicate that such a change is desirable.

Contracts may be awarded for the long-term investigation of broad objectives relating to a specific process, technique, or technology; or they may be for short-term, desktop evaluations providing expert opinion and analysis of the applicability of a process before larger sums are committed for experimental work.

Contracting Procedure

Ideas related to advanced waste treatment that prove worthy of investigation under a formal research contract may be initiated by either the AWTR Program or by an individual or research group having a particular interest or recognized competence in a given field. Either the Program contacts prospective contractors, or prospective contractors present their proposals to the AWTR Program as the initial step in developing a contract.

All proposals that have the potential for developing into research contracts, regardless of the originator, are reviewed in detail by the AWTR staff, frequently with the support and advice of consultants and other authoritative advisers. If the proposal is to be given further consideration, a priority number is assigned and it is ranked with other projects or proposals.

On proposals chosen for support, a detailed plan of research is developed through discussions between the AWTR staff and the selected contractor. The jointly agreed-upon scope of work is compiled into a formal document outlining the specific objectives, the exact area to be studied, the step-by-step methods, and the needs for equipment and personnel. This outline is then submitted to the PHS Contracting Officer for administrative processing. Upon execution of a contract, the contractor is authorized to proceed. Reimbursement is normally made at regular intervals on the basis of itemized vouchers submitted to the

Government by the contractor. Final payment is generally made upon acceptance of a final report covering the work performed.

DIRECT RESEARCH BY AWTR STAFF

Research undertaken in PHS laboratories or otherwise supervised directly by AWTR staff members is referred to as direct or in-house research to distinguish it from contract research. Direct research has involved primarily laboratory studies, but field investigations have increased during the past year as different processes approach the stage for pilot scale investigation.

Laboratory Studies

Most of the direct laboratory research is done at the Robert A. Taft Sanitary Engineering Center and embraces a growing number of projects involving many aspects of physical and chemical separation techniques as well as identification and measurement of organic and inorganic pollutants. Projects may involve only a brief study of a specific detail or, more often, a detailed evaluation of some phase of waste-water renovation that may be needed to assess the technical or economic feasibility of a process. In certain instances, experiments are made to confirm results and conclusions submitted by contract researchers. In addition to supporting the contractors' findings, these permit the PHS researcher to apply his background and special competence to appraisal of the AWT technique in question. Direct research may also include studies to develop special analytical procedures or experimental techniques and evaluate new analytical instruments or devices; special experiments are also undertaken sometimes to support a current or previous line of research and thus help determine the best course for future efforts.

A critical function of this phase of the AWTR Program is to provide various types of laboratory and analytical support to contractors, especially those who may have had little or no experience in making analyses on waste streams. By developing standards for analytical methods and conducting verification analyses from time to time, much contractor time is saved and errors are prevented from creeping into analytical procedures or interpretations of routine results.

Field Studies

During the past 2 years an increasing number of field studies have been undertaken as a part of the AWTR direct research activities. By the time a candidate treatment process has reached the evaluation stage, it is most advantageously evaluated at an actual municipal waste treatment plant where a continuous flow of primary or secondary effluent is available. This phase of advanced treatment technology development is carried out by AWTR staff members through cooperative agreements with municipalities, sanitation districts, and so forth. The projects may be staffed entirely by the Program or jointly with plant personnel.

SEPARATION PROCESSES

Many different types of re-use are anticipated for renovated waste waters. For each proposed usage, the quality requirements for the product water with respect to organic and inorganic composition may vary widely. Moreover, individual AWT processes do not necessarily have to achieve complete removal of all contaminants or even complete removal of a single contaminant to be considered successful or usable. Since waste-water renovation will be patterned to meet any of a variety of re-uses, the relative effectiveness of a number of separation processes must be thoroughly explored and their capabilities demonstrated so that optimum systems may be selected.

It is the policy of the AWTR Program to consider any prospective separation process, even though it may appear completely unconventional. These processes are given at least desktop exploratory evaluations before being accepted or rejected. Any process that shows probable economic and technical feasibility on its initial consideration or at any stage of development thereafter is pursued through as many subsequent stages of laboratory study, pilot plant testing, or field evaluation as it merits.

During the past 2 years, work has progressed at various stages of development on several separation processes that have been judged suitable for further study. The processes that have shown the most promise have been vigorously pursued. The level of development of each process and the progress made on each are reported in the following pages.

Adsorption

The occurrence in municipal waste water of organic contaminants resistant to biological degradation presents the major technical challenge in advanced waste treatment. For many re-use applications these materials must be reduced in concentration or completely removed; furthermore, their presence can seriously interfere with other stages of treatment either for inorganic removal or disinfection.

Removal of these residual organics becomes, therefore, a critical aspect of advanced waste treatment, requiring separation techniques that will be suitable for reducing the comparatively large concentrations of refractory organic compounds occurring in secondary effluents (50 to 100 ppm COD) and that can effectively scavenge organics at the 3— to 5-ppm concentrations. This latter requirement would occur after an advanced treatment process that has been only partially effective in removing organics and that must, therefore, be supplemented by a final polishing of the effluent to meet the highest quality standards.

Past experience points to adsorption as a very effective method of achieving organic removal from aqueous solutions. Owing, however, to the lack of specific experience in adsorbing organics from waste streams and to the variable composition and concentration of organics encountered in waste streams, it has been necessary to conduct a rather broad program of research to obtain a thorough understanding of adsorption in this application.

Activated carbon has been fairly widely used in the treatment of domestic water supplies for taste and odor removal; hence, some information is available about the effectiveness of certain active carbons in removing relatively small concentrations of organics from water. This application has also indicated the practicability of carbon's contacting relatively large volumes of water containing small contaminant concentrations.

In expanding this rather limited background, the AWTR Program has undertaken an extensive evaluation of adsorption in general with particular emphasis on activated carbon. This research has included laboratory scale studies by the AWTR staff and work by several contractors having special talents and knowledge in the particular aspect of the problem they investigated. The areas covered to date have included adsorption kinetics of activated carbon, organic removal efficiencies of powdered and granular activated carbon, and engineering feasibility of organic removal from primary and secondary effluents before and after filtration. Studies have also sought to establish the feasibility of regenerating spent carbon to drive off the adsorbed materials and permit its re-use. The adsorptive capacities of various other materials have been studied, and the possibility of modifying coals and other comparatively low-cost carbon-containing compounds to increase their adsorptive capacities has been considered.

KINETICS OF ADSORPTION

Under a contract with Harvard University, a project was undertaken in May 1961 to characterize the adsorptive phenomena in synthetic experimental systems of selected biochemically resistant organic compounds and solid adsorbents. This research, emphasizing the study of adsorption of model compounds such as alkyl benzene sulfonates (ABS) and other resistant materials, was intended to develop a more complete understanding of rates of adsorption in these systems and evaluate the prospective worth of adsorption on carbon as a method of achieving removal of refractory compounds from waste waters.

The solutes investigated are among those biochemically resistant materials often found in conventionally treated waste-water effluents and in receiving waters into which these effluents are discharged. These include ABS, octyl phenoxyenneaethoxyethanol, and nitrochlorobenzenes.

The experimental procedure involved a batch operation in which the granular carbon and the test solution were continuously stirred in a glass container, samples being withdrawn at appropriate intervals for analysis. Initial testing was done with pure compounds of sulfonated alkyl benzenes, but later studies included tests with technical-grade and reagent-grade benzene sulfonates and with phenol.

In selecting a suitable carbon to be used for the main experimental work of the study, several commercially available carbons were tested. These were derived from a variety of materials including wood charcoal, lignite, and cocoanut shell. They were divided into two size classifications (having mean particle diameters of 0.276 and 0.126 mm) and subjected to an evaluation of pertinent physical properties including comparative adsorption capabilities for (2-dodecyl) benzene sulfonate from aqueous solutions. Columbia LC Carbon, a relatively hard, abrasive-resistant material produced from cocoanut shell was selected as the adsorbent to be used. The rate of uptake of sulfonated alkyl benzene by the candidate carbons screened is shown by the curves in Figure 1.

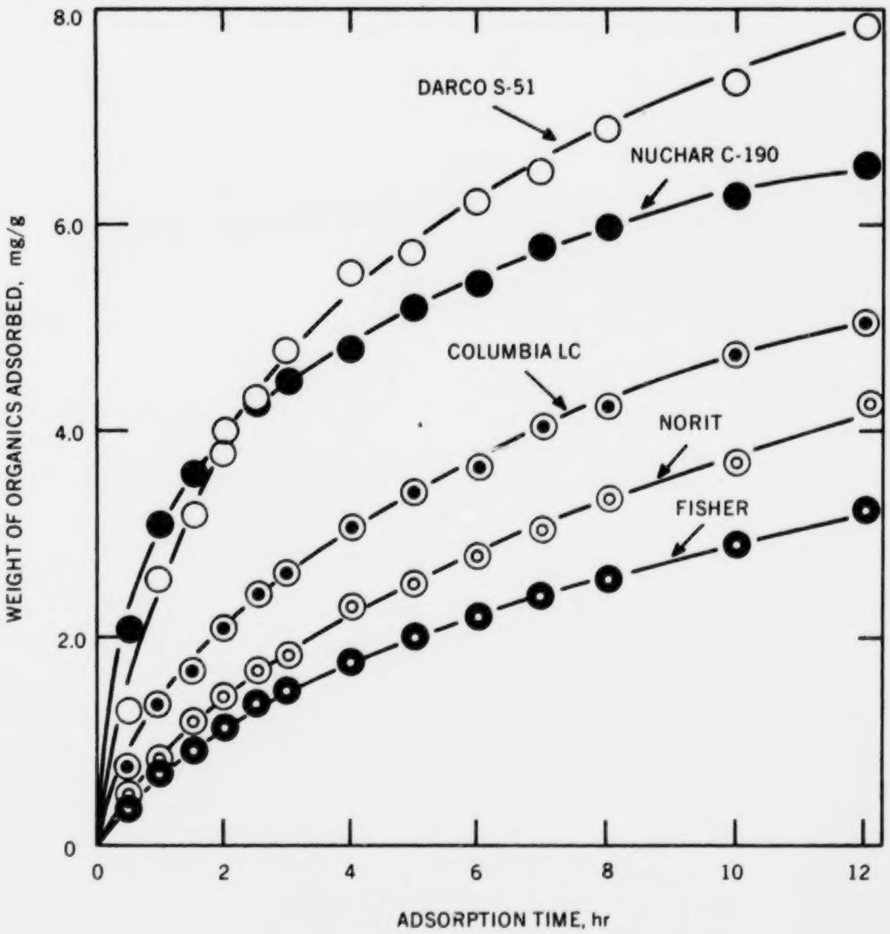


Figure 1. Adsorption rates for selected carbons from aqueous solutions of (2-dodecyl) benzenesulfonate in batch-type systems; 30°C, 75.0 mg/liter, 0.273 mm activated carbon, $C_0 = 10$ mg/liter.

The detailed testing program involving single-solute systems was carried out to establish relationships among rate and capacity of adsorption and surfactant concentration, temperature and pH of the solution, contact time, size and structure of the adsorbate molecule, and size of carbon granules.

The principal findings of this investigation of batch-type systems are as follows:

1. Adsorption proceeds much more slowly than anticipated.

2. Rate of adsorption appears to be controlled by the rate of diffusion of solute within the internal capillary pores of the granular carbon particles.

3. Rate of uptake of ABS by granular carbon increases with decreasing pH of the solution.

4. Rates of adsorption increase with increasing concentration of solute, but adsorption of ABS from water is relatively more rapid the more dilute the solution. This is advantageous for the removal of final traces of material in the renovation of a waste water.

5. Rate of adsorption per unit weight of material adsorbed decreases considerably as molecular size increases.

6. The structure of the alkyl chain attached to the benzene ring has a small but measurable influence on the rate of adsorption; molecules having a highly branched structure are removed more slowly than straight-chain or more nearly straight-chain molecules.

7. Relative adsorption rates vary reciprocally as the square of the diameter of the individual carbon particles in adsorbing surfactants.

8. Temperature effects on adsorption equilibria are generally felt not to be significant over the range of temperature practically encountered in water and waste waters.

In evaluating other commercially available carbons to establish the suitability of adsorbents that may be less expensive than the Columbia LC Carbon, Pittsburgh carbon (a relatively soft carbon) was found to exhibit a rate constant for adsorption of technical-grade ABS about five times as large as that for the Columbia LC Carbon. This increased capacity is presumably attributable to larger pore diameters of the Pittsburgh carbon. Because of their high capacity and high rate of uptake, these larger pore carbons appear more suitable for application to waste-water treatment.

Despite the recognized effectiveness and superiority of activated carbon as an adsorbent for the treatment of aqueous solutions, its proposed use for the treatment of larger volumes of waste water presents two major difficulties. The first is its relatively high cost and the second is the difficulty of regenerating typical water-grade carbons because of their fragility. In recognition of these problems, a continuing effort is directed toward a search for possible alternative adsorbents. As part of the study on kinetics, a few preliminary adsorption tests were made on three possible adsorbent materials selected for their relatively low cost, availability as waste materials, and prospective adaptability to regeneration. These were (1) fly ash produced in the generation of gas from coal, (2) ash from the incineration of sewage sludge, and (3) an activated aluminum oxide produced by controlled dehydration at about 500°C.

Results from using the two forms of ash indicated that these materials are unsuitable as adsorbents for general treatment of waste waters because adsorption capacities were very low. On the other hand, the results with activated aluminum oxide were promising in regard to adsorption of (2-dodecyl) benzene sulfonate. Adsorption capacity of the bauxite approached that of the Columbia carbon on a volume comparison basis, but the greater density of bauxite compared with that of activated carbon must be kept in mind when comparing the two materials. If the bauxite shows equally good adsorption properties for other substances, and if it is shown to be readily regenerable, it could well be a candidate material for waste-water renovation.

ADSORPTION IN COLUMNS OF FLUIDIZED MEDIA

A particularly significant finding in the studies of adsorption kinetics in single-solute, batch-type systems involving principally ABS was that the rate of organic uptake varied as the inverse square of the diameter of the activated-carbon particles. From this it appears desirable to keep particle sizes as small as possible to attain high rates of adsorption.

As a followup to the fundamental studies on kinetics, an investigation was undertaken to evaluate fine particulate adsorbents in a column-type contacting apparatus employing continuous flow of the test liquid. To avoid the problem of excessive headloss common to standard packed-bed operation with fine media (where a down-flowing liquid is used), a fluidized-bed operation was used wherein the waste water flowed upward through an expanded bed of the fine particulate adsorbent. This technique of suspending the solid particles in the upflowing liquid eliminates, or at least reduces, the difficulties of air binding and fouling with particulate matter. The arrangement of equipment used in this study is shown schematically in Figure 2. The lucite tube containing the test adsorbent was 1 inch in diameter by 3 feet long. Adsorption beds contained about 8 to 9 inches of settled material, which, when fluidized, occupied approximately twice the settled volume.

The laboratory study was directed toward the definition and evaluation of adsorptive characteristics in fluidized media. The kinetics of adsorption were investigated in terms of organic uptake profiles relative to the velocity dimensions, time and length, for selected values of these variable and for variously sized particles of absorbent. Following the pattern of the batch-type studies, these column studies used only single-solute solutions to facilitate interpretation of the relative significance of more fundamental variables.

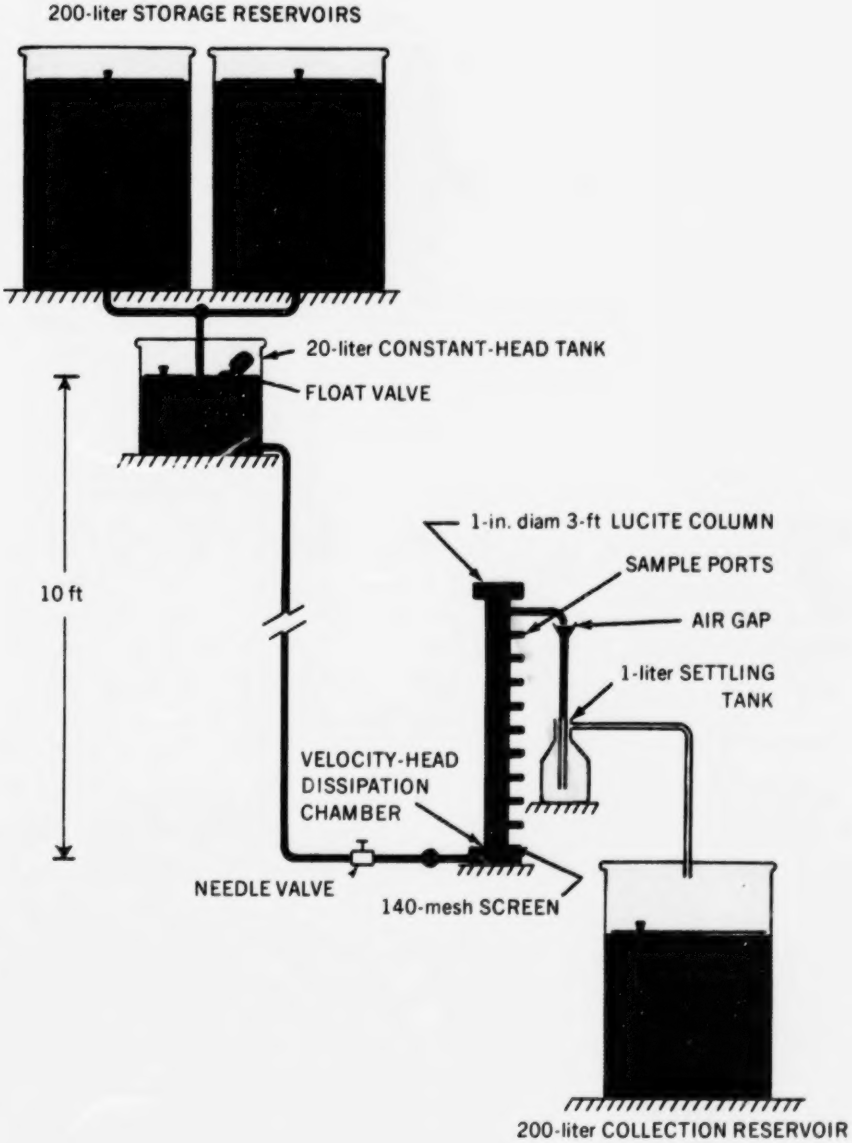

200-liter STORAGE RESERVOIRS
20-liter CONSTANT-HEAD TANK
FLOAT VALVE
10 ft
1-in. diam 3-ft LUCITE COLUMN
SAMPLE PORTS
AIR GAP
1-liter SETTLING TANK
VELOCITY-HEAD DISSIPATION CHAMBER
NEEDLE VALVE
140-mesh SCREEN
200-liter COLLECTION RESERVOIR

Figure 2. Schematic diagram of experimental apparatus for studying adsorption kinetics in fluidized media. Activated carbon and activated aluminum oxide were studied in this upflow-column-type contactor to evaluate the adsorptive characteristics of fine particulate adsorbents in single-solute systems – in this case alkyl benzene sulfonate.

Technical-grade ABS was used as the adsorbate in all tests. Adsorbents studied included two granular activated carbons and an activated aluminum oxide. The granular carbons used were the relatively hard Columbia LC and the softer Pittsburgh carbon tested previously. These were in eight particle sizes whose mean diameters ranged from 0.126 to 0.503 millimeter, except in one study that used 1.545-millimeter particles.

To compare upflow and downflow columns using fine particles, a few experiments were conducted with unexpanded downflow columns; these tests were identical in all other respects to the tests with expanded beds. Despite the use of relatively large particles of carbon (0.359 and 0.276 mm), the downflow studies were unsuccessful and produced no comparative data. In these tests, the flow rate dropped to less than one-half the initial rate after 24 hours and to one-tenth the initial rate within 30 hours.

Adsorption of organic material appeared to increase the density of the carbon adsorbents studied in upflow columns, making it necessary to increase continuously the rate of liquid flow up through the carbon bed to maintain the same degree of expansion. Since the nearly saturated particles were lifted less than fresh particles were in this situation, there was a stratification in the bed with nearly exhausted adsorbent at the bottom at the point of inflow. This created a measure of countercurrent contact since withdrawal of particles from the bottom of the bed mostly removed the substantially saturated carbon.

Column experiments involving the fine-particle carbon (0.178 mm) showed almost 80 percent realization of available capacity at the arbitrarily selected breakthrough point ($c/c_0 = 0.3$), while coarse-particle (0.503 mm) material had reached only 10 percent of available capacity.

Other significant trends indicated by the results of expanded-bed studies are as follows:

1. Total solute adsorbed per unit weight of adsorbent increases as particle size of carbon decreases (within the limits of the breakthrough point).

2. Total solute adsorbed per unit weight of adsorbent increases as flow rate of solution decreases (within the limits of the breakthrough point).

The findings from these expanded-bed studies must be interpreted in light of the very shallow beds studied (8 to 9 inches of settled carbon) and the relatively high flow rates employed, the range being from 0.7 to 6.1 gallons per minute (gpm) per square foot. Additional data of this type employing deeper beds will be valuable.

FIXED-BED CARBON TREATMENT OF SECONDARY EFFLUENTS

A study in which granular activated carbon was used in fixed-bed contactors was carried out by the Research and Development Department of Pittsburgh Chemical Company. It was done to establish optimum adsorption bed depth and flow rates necessary for achieving maximum economic use of the adsorptive properties of the carbon, as well as the feasibility of regenerating carbon for re-use by thermal reactivation.

First, a bench scale study was set up wherein a continuous stream of effluent from a municipal activated-sludge plant was passed through a fixed bed of carbon. The test column contained 20 feet of granular carbon in a 2-inch-diameter pyrex pipe, arranged by connecting four separate 5-foot columns in series (Figure 3). A high-capacity, liquid-phase granular carbon (Pittsburgh Type SGL) with a comparatively large surface area was used. Particles were sized to pass a 2.38-millimeter sieve and be retained on a 0.59-millimeter sieve. On the initial test, a flow rate of 10 gpm per square foot of cross-sectional bed area was used. The chlorinated and sand-filtered feed was pumped downflow under pressure through the system at a constant flow rate.

Secondary effluent was passed continuously through the carbon until adsorption efficiency diminished, permitting ABS to pass through the column in trace amounts. The test was continued until the ABS content

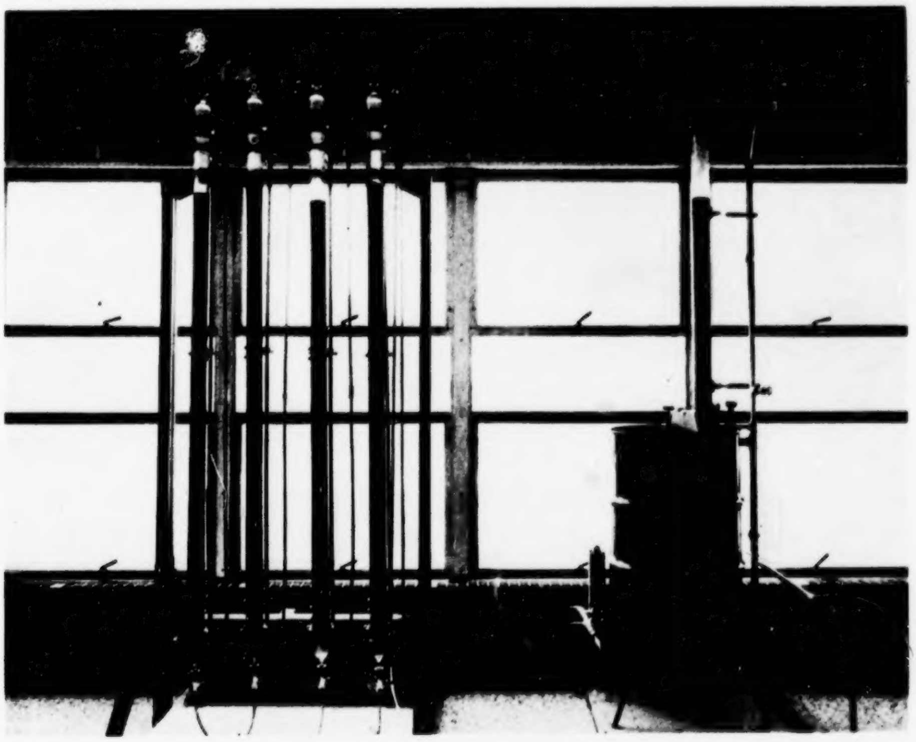


Figure 3. A 20-foot carbon column, composed of four separate 5-foot sections connected in series, was used to study the effectiveness of activated carbon as an adsorbent for organic contaminants contained in secondary municipal waste-water effluent under continuous-flow conditions. As the carbon became exhausted, it was regenerated in one section at a time and its usage continued.

in the effluent from the fourth column had increased to 0.5 ppm. At this point the system was shut down and the carbon in the first column was removed and thermally reactivated. The reactivated carbon was recharged to the empty column, which was then installed in the number 4 or final position in the series. The study was terminated when this procedure had been repeated three times.

Even at the high flow rate of 10 gpm per square foot, the 20-foot carbon column proved very effective in removing ABS and other organics (measured by the COD test). The secondary effluent entering the carbon column averaged approximately 50 ppm COD and 5 to 6 ppm ABS. These COD and ABS concentrations were reduced to 12 to 20 and less than 0.5 ppm, respectively. If the COD "leakage" was due to unadsorbed organic matter in solution, increased liquid residence time should effect a more complete removal. Consequently, the test was repeated at a flow rate of 4 gpm per square foot. Nevertheless, though the influent concentration of 72 ppm COD approximated the previous test condition, the lower flow rate reduced organic content to an average COD of only 18.5 ppm. This was no better than the 12 to 20 ppm values obtained previously. Filtration tests with membrane filters showed that the residual COD was not due to suspended solids. The presumption is, therefore, that the material is either colloidal or very difficultly adsorbable, soluble organic matter.

Because of these results, the carbon application rate (i.e., the carbon regeneration rate) needed to achieve the amounts of organic removal demonstrated is estimated to be less than 1 pound per 1,000 gallons of secondary effluent for the 10-gpm flow rate and approximately 0.75 pound per 1,000 gallons of secondary effluent treated for the 10-gpm flow rate.

REGENERATION OF GRANULAR CARBON USED FOR TREATMENT OF SECONDARY EFFLUENT

Thermal Regeneration

The spent carbon from the 20-foot adsorption column used in treating filtered secondary effluent was reactivated in a pilot scale rotary furnace having a capacity of about 3-1/2 pounds of carbon. The regeneration was carried out at 1,700° F in an atmosphere of 34 percent steam and 66 percent air; required retention time was 14 minutes. The carbon used in the 20-foot column test and reactivated only once was restored to essentially virgin adsorption activity despite a 6 to 9 percent increase in its total ash content. In a subsequent study, a single 5-foot column of the same Pittsburgh-type SGL activated carbon was subjected to six cycles of exhaustion and regeneration. Each involved exhaustion of the carbon to the degree that might be expected in practice by the continued passage of secondary effluent through the column. In this test the ash content of the carbon increased by about 20 percent on the first cycle, and at the end of six complete cycles, the carbon contained 70 percent more ash than it had originally. Although insoluble in water, the ash is predominantly acid soluble. The adsorptive properties of the carbon, as measured by standard activity tests, were not, however, appreciably impaired by this ash buildup. The amount of carbon lost during the six-cycle reactivation study amounted to 4.4 percent per cycle, falling within the anticipated 3 to 5 percent range.

The effect of further ash buildup on the adsorption capacity of carbon through extended cycles of exhaustion and regeneration has not been clearly defined by these limited-cycle tests. To make such a determination will require a study in which the cyclic exhaustion and reactivation of the carbon is continued until there is no further decrease in activity with successive cycles.

Preliminary studies, in which accelerated batch-type reactivation tests were carried out by adsorbing ABS from dilute single-solute solutions, have established that granular carbon, alternately loaded with Ca-ABS and thermally reactivated for 10 complete cycles, doubled the ash content of the carbon and reduced its adsorption capacity for ABS from dilute solutions to approximately one-half its virgin capacity. In these tests the ash proved insoluble in water but soluble in acid. If it becomes necessary to prevent this ash buildup in practice, acid treatment of the carbon after thermal reactivation would be required. Since ABS represents, however, only a fraction of the total organics in secondary effluent, the data on buildup of ash from the synthetic ABS solutions used in the laboratory studies cannot be considered as completely representative of what can be expected from the secondary effluent itself.

Chemical Regeneration

In view of the comparatively high cost of activated carbon, various methods of reactivation, including chemical oxidation, have been considered to establish the most effective and most economical method of providing for re-use of the carbon. In a study carried out by the Dow Industrial Service Division of Dow Chemical Company, a number of commercially available chemical oxidants were screened for preliminary evaluation of their ability to regenerate activated carbon that had been partially exhausted by passage of a sand-filtered, activated-sludge effluent. The activated carbon used was Cliffs Dow, 10 by 30 mesh.

The following oxidants were evaluated: Chlorine, bromine, potassium permanganate, sodium dichromate, sodium persulfate, potassium persulfate, sodium peroxide, hydrogen peroxide, and ozone. The oxidant regeneration studies were carried out by pumping the oxidant solutions up through a column of the exhausted activated carbon. The experimental equipment used is shown schematically in Figure 4.

Regenerative efficiency of the individual oxidants was rated on the adsorptive capacity achieved with a regenerated carbon in comparison with that achieved by a virgin carbon sample in treating the same waste effluent. The results obtained with the different oxidants are shown in Table 1.

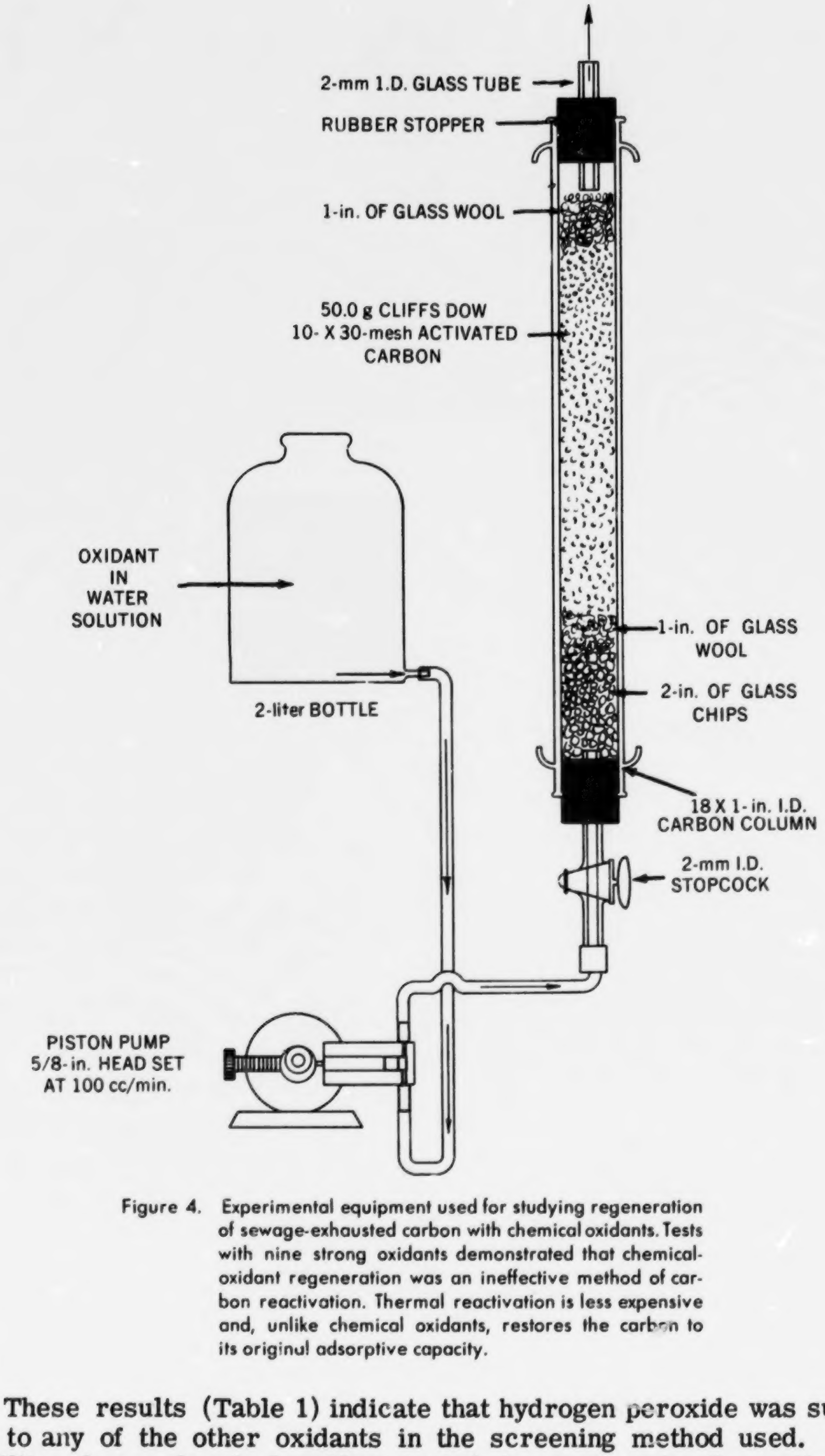

2-mm I.D. GLASS TUBE
RUBBER STOPPER
1-in. OF GLASS WOOL
50.0 g CLIFFS DOW 10- X 30-mesh ACTIVATED CARBON
OXIDANT IN WATER SOLUTION
1-in. OF GLASS WOOL
2-in. OF GLASS CHIPS
2-liter BOTTLE
18 X 1-in. I.D. CARBON COLUMN
2-mm I.D. STOPCOCK
PISTON PUMP 5/8-in. HEAD SET AT 100 cc/min.

Figure 4. Experimental equipment used for studying regeneration of sewage-exhausted carbon with chemical oxidants. Tests with nine strong oxidants demonstrated that chemical-oxidant regeneration was an ineffective method of carbon reactivation. Thermal reactivation is less expensive and, unlike chemical oxidants, restores the carbon to its original adsorptive capacity.

These results (Table 1) indicate that hydrogen peroxide was superior to any of the other oxidants in the screening method used. The inability of any chemical oxidant tested to regenerate the activated carbon completely to its original state could be due to any of a number of factors. Causes could include site poisoning, rate of reaction with the contaminant, blocking of micropores either by gas or oxidation products, low diffusion rate of oxidant or product, degradation of active sites by the oxidant, and so forth.

Table 1. OXIDANT REGENERATION EFFICIENCIES ON CLIFFS DOW 10- x 30-Mesh ACTIVATED CARBON

Oxidant	Oxidant concentration, %	Average regeneration efficiency, % 1st Regn.	2d Regn.	3d Regn.
Chlorine water	0. 46	15	0	--
Bromine water	3. 50	10	0	--
$KMnO_4$	10. 00	16	0	--
$Na_2Cr_2O_7$	10. 00	61	20	--
$K_2S_2O_8$	0. 75	49	20	0
$Na_2S_2O_8$	0. 75	55	20	0
O_3	4. 00	25	0	--
Na_2O_2	1. 00	60	20	0
H_2O_2	3. 00	71	50	20

Although the regenerative efficiency of hydrogen peroxide is relatively high for a single-cycle regeneration, the projected cost of this type of treatment even at this efficiency would probably rule it out as a possible regeneration method. The hydrogen peroxide required to regenerate 1 pound of activated carbon would cost over 50 cents, which is about twice the cost of the carbon. Discarding the exhausted carbon would, therefore, be cheaper than regenerating it chemically.

COST OF GRANULAR CARBON TREATMENT OF SECONDARY EFFLUENT

Preliminary cost estimates have been made for a 10-mgd treatment plant based on present knowledge of the adsorptive capacity of carbon and its regeneration possibilities. The proposed design is based on a 4-gpm-per-square-foot flow rate through the carbon bed and a 0. 5 ppm ABS breakthrough to determine the time at which the carbon would be thermally regenerated. Under these conditions, treatment costs are expected to be about 10 cents per 1, 000 gallons of effluent treated. Additional expense, for removing suspended solids from the feed, could amount to 6 to 7 cents per 1,000 gallons. Unit treatment costs in a 100-mgd plant are expected to be about 7 cents per 1, 000 gallons of treated effluent for the adsorption step and possibly 5 cents additional for solids removal.

GRANULAR CARBON TREATMENT OF PRIMARY EFFLUENT

In a single test, primary effluent was first passed through a sand filter as preconditioning for treatment in a granular-carbon bed 20 feet in depth. Type SGL Pittsburgh activated carbon was again used. Particles passed a 2.38-millimeter sieve and were retained on a 0.59-millimeter sieve. The average concentrations (in ppm) of the contaminants in the sand-filtered primary effluent before entering the carbon column were ABS 5.6, COD 236, and BOD 154. The carbon treatment reduced these to average ppm values of ABS 0.2, COD 91, and BOD 67. During the test period, the final effluent from the activated-sludge system at the treatment plant had an average BOD of 18 ppm.

Membrane filtration tests showed that a sizable fraction of the residual organic in the effluent from the carbon column could be accounted for by suspended solids that penetrated the carbon bed. The latter were not effectively removed by the sand filter and penetrated the carbon bed to such an extent that rapid increases in pressure drop occurred, which necessitated frequent washing of the carbon and made accurate control of the 10-gpm-per-square-foot flow rate impossible.

The mechanical problems associated with the suspended solids, and the unsatisfactory BOD and COD reductions obtained led to the conclusion that activated-carbon treatment of primary effluent under the conditions tested was not feasible.

USE OF COAL AND MODIFIED COALS AS ADSORBENTS

The relatively high cost of activated carbon gives rise to the need for and desirability of developing or locating granular adsorbents that would be less expensive than activated carbon. Since coal costs about 1/4 cent per pound, this economic advantage makes it particularly attractive as a potential adsorbent and has dictated that it be evaluated for this usage.

Previously mentioned limited exploratory investigations have demonstrated that other low-cost, readily available materials such as ashes from incinerated sewage sludge and flyash produced in the generation of gas from coal was unsatisfactory adsorbents. Work on activated aluminum oxide produced variable results, which appeared to depend somewhat on the iron content of the material tested.

A more nearly complete evaluation has been made of the adsorbent potential of coals and various carbon-containing or coal-derived compounds to test their suitability for removing organics from municipal secondary effluents. At least one type of all the major ranks of coal in this country were tested. In addition, the study has investigated coke, flyash from coal-fired power plants, pretreated coals, and miscellaneous materials including commercial chars, peat, and steel mill slag. The adsorptive capacities of these materials were measured and compared with that of granular activated carbon.

Many of the coals and coal-derived materials were shown to possess some degree of adsorptive capacity for organic contaminants in waste waters, but others were ineffective; some of the coals even added organics to the waste water, which increased the content of organics as measured by the COD test. One of the coals tested by repeated contact with fresh effluent was shown to have about one-fourth the capacity of activated carbon for removing COD-measured organics, adsorbing about 4 percent of its weight before it became saturated. In addition to its initial cost advantage, coal has the further advantage that it can be burned after being used as an adsorbent with no loss in fuel value. Furthermore, burning of the coal as a fuel also achieves the ultimate disposal of the adsorbed wastes without requiring additional plant facilities. Some of the flyashes tested by a single 24-hour contact were very effective as adsorbents, removing as much as 66 percent of the organics and 76 percent of the ABS present in the waste water. These removals occurred at the highest adsorbent dose studied (8 grams per liter). The effectiveness of the flyashes improved with their increasing carbon content. Coals pretreated by mild oxidation were ineffective as adsorbents.

This investigation was made by the Pittsburgh Coal Research Center of the Bureau of Mines. The complete list of materials studied included 6 anthracite coals, 12 low-volatile bituminous coals, 14 medium- and high-volatile bituminous coals, 5 sub-bituminous coals, and 1 lignite. Flyash from 17 pulverized-coal-burning power plants was also tested. Twenty pretreated coals were tested including one lignite char. Included in the miscellaneous group of materials studied were two samples of coke and single samples each of Mont char, Disco, coal ash, steel mill slag, Michigan peat, and bituminous char.

The study was carried out with batch-type experiments in which the candidate adsorbents were contacted with filtered secondary effluent contained in glass flasks under controlled temperature conditions. The adsorbate was analyzed for changes in COD, ABS, TDS, pH, and conductivity. Early results indicated only slight changes occurred in TDS, pH, and conductivity of the treated solutions; hence, these analyses were eliminated in subsequent tests. The laboratory equipment used in the experiment is shown in Figure 5. Figure 6 is a photograph of the contacting flask showing the special stirring device designed to prevent the formation of a vortex during agitation.

The initial step was a screening study to ascertain the materials that had sufficient adsorptive capacity to warrant further investigation. Candidate adsorbents were sieved to a 42- to 60-mesh size except for the flyashes and peat, which were tested without size separation. Each of these single-contact tests was made with 3 liters of effluent in a 4-liter flask with 9 grams of adsorbent added to provide an adsorbent loading of 3 grams per liter. Contact time was 24 hours and stirring was continuous. Materials that showed the best adsorptive capabilities were later subjected to further testing with the same 42- to 60-mesh size particles and also with 200- to 250-mesh particles to evaluate a range of adsorbent loadings that included 0.5, 1.0, 2.0, 4.0, and 8.0 grams of adsorbent per liter of effluent. This more intensive evaluation of the most promising adsorbents screened from the original 84 materials was made on 15 materials including samples of activated

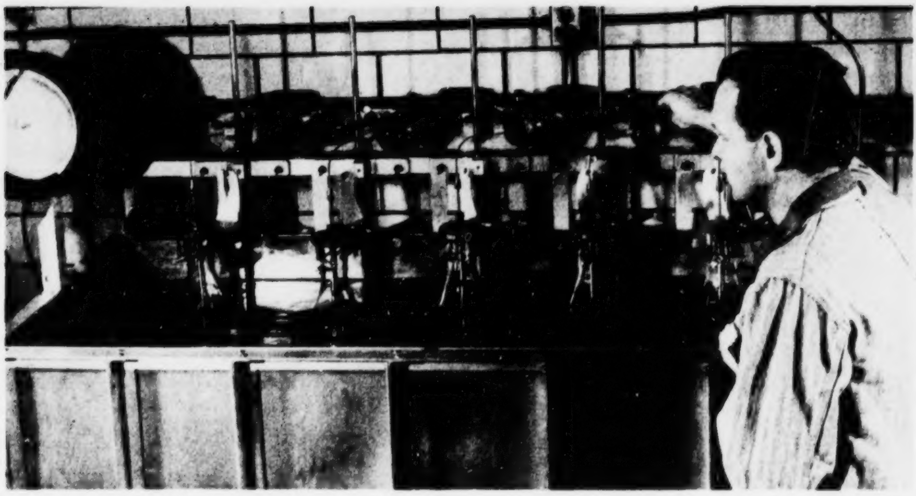


Figure 5. Laboratory equipment used for experimentally contacting coal and other potential adsorbents with secondary sewage effluent to evaluate their capacities for adsorbing organic contaminants. Although activated carbon is an excellent adsorbent for organic wastes, a search is continuing for less expensive adsorbents.

carbon, which provided a basis for comparing the effectiveness of the other materials. Included among the intensively studied samples were one anthracite coal, four bituminous coals, three sub-bituminous coals, one lignite, four flyashes, and one pretreated coal.

Results obtained for the different coals and other materials tested are as follows:

Anthracite Coal

Anthracite coals were generally poor adsorbents. The 8-gram-per-liter adsorbent concentrations produced reductions in COD values of 53 and 36 percent respectively for the 200- to 250-mesh and the 42- to 60-mesh particles. Progressively greater removal of organics was observed with increasing concentrations of the granular anthracite coal, a relationship that did not hold true for most of the bituminous coals.

Low- and Medium-Volatile Bituminous Coal

Organic removal was relatively poor for low- and medium-volatile bituminous coal. Poor reproducibility of results indicated the possibility of nonuniform composition in the coal samples. Adsorbent concentrations above 2 grams per liter produced no significant increase in contaminant removal.

High-Volatile Bituminous Coal

Although most of the high-volatile bituminous coals showed comparatively poor adsorption capabilities, 4 of the 12 samples produced better than 30 percent reduction in COD. One of these removed an

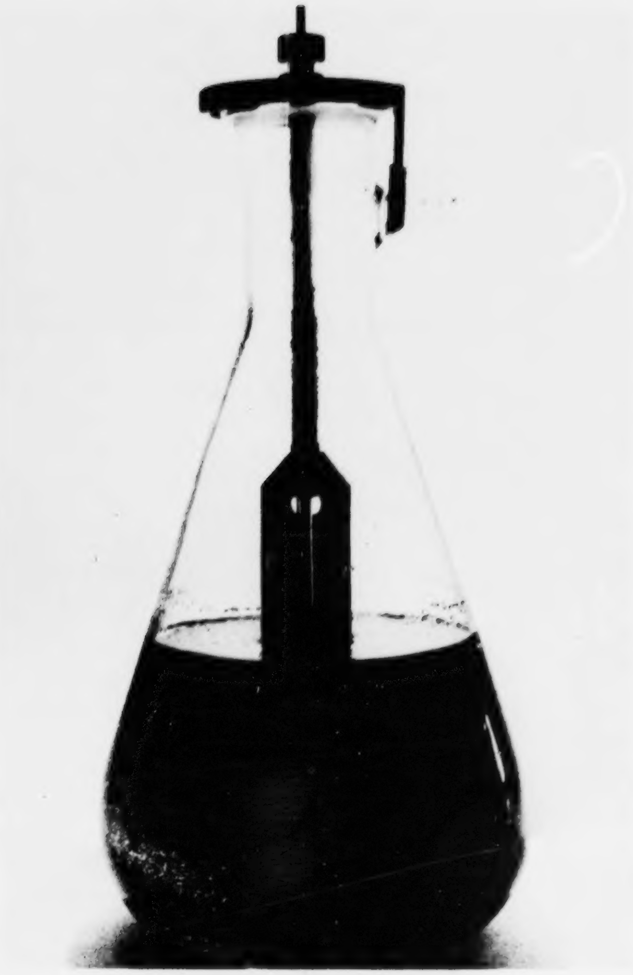


Figure 6. Flask containing secondary sewage effluent and powdered coal illustrates method used for screening candidate adsorbents in evaluating their adsorptive capabilities. The special stirring paddle, designed, to eliminate a vortex and provide better liquid-solid contact, agitates mixture continuously during 24-hour test period.

average of 44 percent of the COD-measured organics at the 3-gram-per-liter concentration. Individual results for this one sample coal ranged, however, from 21 to 64 percent with a standard deviation of 14.7 percent removal. Several of the high-volatile coals contributed organics with the result that COD measurements of the treated effluent were higher than those of the untreated effluent. Reproducibility of results was comparatively poor.

Sub-bituminous Coal

Sub-bituminous coals were generally poor adsorbents and showed rather wide variations in adsorption capacity on the limited number of tests conducted. One sample, sub-bituminous coal C[†], contributed 17 ppm organic matter (COD) at the 2-gram-per-liter dosage.

Lignite

Tests with lignite produced either very small COD reductions, or the lignite added organics to the sample and increased the COD measurements.

Flyashes

In general, flyashes were fairly good adsorbents, producing COD-measured organic reductions that ranged from 17 to 83 percent on the 17 samples tested. Six of the more effective flyashes, four from large pulverized-coal-fired power plants, were subjected to intensive testing at five concentrations. In these tests, the maximum adsorbent concentration of 8.0 grams per liter produced COD reductions ranging from 48 to 66 percent and ABS reductions ranging from 49 to 87 percent. The smallest adsorbent concentration tested, 0.5 gram per liter, produced COD reductions ranging from 9 to 21 percent.

In general, increased adsorbent concentration produced increased contaminant removal within the ranges studied. In this respect the test results with flyash were much more consistent than those with coals. Virtually no organic material, as evidenced by COD measurements, was contributed by the unsieved flyashes. They settled out as readily as coal after stirring ceased. Settling of the adsorbents was aided by the wetting ability of the ABS in the effluent, as noted by comparing the settleability of the adsorbents in the distilled water blanks.

Flyash samples were not sieved to specific size ranges, as were the other materials tested, but were used as received. In general, the effectiveness of flyash as an adsorbent is dependent on the amount of carbon it contains, its effectiveness increasing with the carbon content. Carbon content in the flyashes studied varied from 0.1 to 35.3 percent but the latter figure is not representative of acceptable commercial, operation for large pulverized-coal-fired furnaces. Note, however, that, despite the operating goal of low-carbon flyash, several of the commercial power plant flyashes tested contained greater than 15 percent carbon.

The use of flyash as an adsorbent for waste-water treatment could conceivably provide an attractive application for this waste product, which currently presents a costly disposal problem to power-generating stations. This application would, however, complicate rather than resolve the final disposition of the flyash. Adsorption would leave the material coated with organic matter and would not reduce the volume or change the composition of the original material.

Pretreated Coals

Various temperature and pressure combinations were applied to the partial treatment by oxidation and volatilization of raw coal in an effort to develop an adsorbent more efficient than the raw coal but less costly than activated carbon. Treatment temperatures ranged from

400° to 900° C; pressures included atmospheric and 300 psig; treatment gases included oxygen, steam, nitrogen, and carbon dioxide in varying mixtures and concentrations.

Most pretreated coals were slightly better adsorbents than the same untreated coals were, but the slight advantage realized was not sufficient to warrant continuation of this phase of the study.

Miscellaneous Materials

Included under miscellaneous materials were several commercial chars and cokes, coal ashes, steel mill slag, and Michigan peat. None were efficient adsorbents for organic wastes. The Michigan peat contributed organics, which amounted to a 55 percent increase in the COD measurement after contact.

Activated Carbon

Pittsburgh Chemical Company-type SGL activated carbon was tested along with the other materials to provide a reference background for comparison. Both 42- to 60-mesh and 200- to 250-mesh particles were used. COD removals were considerably better than for most coals, ranging from 74 to 94 percent. ABS removal ranged from 92 to 97 percent.

Effects of Multiple Contacts of HVCB Coal to Establish Saturation Level

A sample of the high-volatile-C bituminous coal, which had proved to be a relatively good adsorbent on the single-contact 24-hour test, was subjected to 10 repeated contacts with fresh effluent after each 24 hours of stirring, to determine how rapidly the coal lost its effectiveness as an adsorbent. The repeated application of fresh effluent demonstrated that this coal was capable of adsorbing 4 percent of its weight of organics as measured by COD and 0.4 percent of its weight of ABS. By comparison, activated carbon adsorbed about 10 percent of its weight of organics and 1.2 percent of its weight of ABS in 10 separate 24-hour contacts with fresh effluent. Even 10 contacts, however, did not saturate the adsorptive capacity of the activated carbon.

Summary

The data obtained demonstrated that the rank of a coal is not a factor related to the adsorption of waste-water refractory contaminants. One coal of a certain rank can be a comparatively good adsorbent while another of the same rank is completely ineffective (rank, according to the ASTM method of classification, is based on the content of volatile matter and fixed carbon). Several coals showed a fairly good adsorption capacity, though none was comparable to activated carbon.

USE OF MINERALS AND CLAYS AS ADSORBENTS

As part of the search for low-cost adsorbents, a study was undertaken to screen a wide variety of inexpensive and readily available materials that might prove suitable for the treatment of waste streams. Materials of particular interest included industrial by-products and scraps, as well as naturally occurring minerals, clays, earths, and the like.

The materials selected for evaluation were obtained mostly from commercial suppliers and manufacturers as finely ground particulates with a mean particle size of approximately 325 mesh, with a range from 200 to 400 mesh. Testing procedures included batch or jar tests, the candidate adsorbents being contacted individually with 500-milliliter samples of chlorinated and filtered secondary municipal effluent in 600-milliliter beakers. The mixtures were paddle agitated at 50 rpm for 50 minutes after which the treated effluent was filtered; the filtrate was then evaluated for organic removal by means of COD measurements.

Suitability as an adsorbent was based on the extent to which the tested materials reduced the organic content of the effluent as measured by the COD tests. The principal findings are summarized as follows:

Metal Oxides

Five metal oxides including calcined and uncalcined bauxite gave insignificant or no COD reductions at dosages up to 4, 000 ppm.

Silicas

Nine silicas including diatomaceous earth, dicalite, celite, and florisil were tested and found to be comparatively poor adsorbents, the largest COD reduction amounting to 10 percent.

Silicates

Twenty silicates tested included materials such as Attacote, Attaclay, Attasorb, greensand, vermiculite, bentonite, and yellow gel. Only two of these showed substantial COD reductions, these being a 35 percent reduction with one sample of Attacote and a 26 percent reduction with one sample of Edgar ASP101. With few exceptions, the other compounds effected an insignificant removal or produced an increase in the COD measurement.

Miscellaneous Materials

Insignificant removals were accomplished by calcium aluminate, limestone, monazite, "rare earth sodium sulfate," one sample of flyash, and one sample of cement stack dust.

Activated Carbon

To provide a basis of comparison for other materials tested, Nuchar C-190-N active carbon was tested by the same procedure at several concentrations; bone black was tested in a single concentration. COD reductions in 14 tests with Nuchar ranged from 20 to 100 percent covering a range of dosages from 200 to 1,000 ppm. The bone black produced only a 23 percent COD reduction at 1,000 ppm adsorbent.

Ion Exchange Resins

Ionac A-540 (Cl^- form) and Ionac A-300 ($SO_4^=$ form) were similarly tested. These produced COD reductions of 94 and 34 percent, respectively.

Modified Adsorbents

Attempts were made to enhance the adsorptivity of certain of these materials by modifying them or by imparting other substances onto them. Several silicates including vermiculite, Wyoming bentonite, and greensand were treated either with a 20 percent aqueous zinc chloride solution or with a 20 percent aqueous solution of hydrous zirconia. The zinc chloride produced little or no improvement in the organic adsorption capabilities of the materials tested in this way. Wyoming bentonite treated with zinc chloride gave a 7 percent reduction in COD but gave a 38 percent reduction when treated with the hydrous zirconia. None of the modifications appeared, however, particularly promising in relation to the results produced by the Nuchar C-190-N.

Chemically Treated Wood Shavings and Sawdust

Attempts were made to convert a wood shaving and sawdust mixture into a cheap adsorbent by two different chemical treatments. The first method involved treatment with a 4.5 percent solution of sodium bisulfite. The second involved treatment of the wood with sodium hypochlorite followed by ammonia.

Secondary effluent subjected to the sodium bisulfite-treated wood shavings showed a 58 to 124 percent increase in COD, the higher increase being produced by higher loadings. Sodium hypochlorite-treated shavings increased the COD readings of the secondary effluent by 12 percent.

Summary

None of the commercially available solid mineral materials and manufacturer's byproducts or scraps tested appeared to offer much promise as possible adsorbents. Note, however, that only one flyash sample was tested, and a more extensive survey of flyashes, previously reported herein, disclosed a number of these materials to be relatively effective adsorbents.

Foam Separation

Foam has assumed the role of a national menace in recent years. Occurring most dramatically in larger accumulations at municipal sewage treatment plants, foam is also frequently found on our lakes and streams and even on tapwater in certain areas. Foam is a by-product of the detergents occurring in municipal waste waters, the most common compound in current use being ABS. Although ABS occurs in relatively small ppm concentrations and accounts for only about 10 percent of the total organic load present in the average municipal waste stream, even this small amount has been judged undesirable because of the public's aesthetic objections to the foam it produces, whether the foam occurs on waste water, on drinking water, or on recreational waters.

The inability of conventional biological sewage treatment processes to decompose "hard" detergents such as ABS accounts for the presence of these detergents in so many waters beyond waste streams. Until the development of a "soft" or completely biodegradable detergent seemed assured, physical separation and removal of foam by deliberate foaming of waste waters appeared to offer the greatest promise of removing the "hard" detergents from waste streams. Considerable experimental work has been undertaken to develop this separation process, and these efforts will, of necessity, continue until the "soft" detergents have actually been marketed and proven to be sufficiently biodegradable in municipal waste treatment plants. If these new compounds, expected to replace existing detergents in the near future, prove to be less than "completely" biodegradable, the physical and mechanical separation techniques developed may still prove to be the final solution to the foam problem.

Regardless of the degree to which "soft" detergents may be biodegradable under conventional usage and waste treatment, foam separation is still expected to provide a useful technique for removal of other contaminants not now removed by conventional treatment processes. This assumes that a certain amount of foam-causing material will remain in municipal effluents, and is based on the fact that a number of other organic materials besides detergents are known to concentrate in a foam and are thereby similarly removed by the foaming process.

FOAMING PRINCIPLE

Foam separation takes advantage of the tendency of surface-active solutes such as ABS to collect at a gas-liquid interface. A large interface area is created by passing air (or gas) bubbles through the liquid. Foaming, per se, provides an efficient means of generating and collecting the gas-liquid interface. When a solution containing surface-active solutes is foamed, the foam becomes enriched with these solutes, and the residual bulk liquid is depleted. The foam can be subsequently collected and collapsed to produce a solute-rich liquid product. In addition to the concentrating of soluble surfactants in surface films, there is also a concentration in the foam of suspended solids by a froth flotation mechanism. Flotation is a very common industrial process, both in mineral beneficiation and even in waste treatment; but, though the literature reports certain industrial uses of foam separation of naturally surface-active substances such as proteins, consideration of the use of foam separation for the treatment of relatively large volumes of liquid, especially for waste treatment, is a rather recent development. Very few attempts at large-scale application of foam separation have been reported.

LABORATORY STUDIES

AWTR investigation of foaming, in the laboratory and in the field, has been aimed at developing practical application of the foaming phenomenon. As a prelude to pilot scale investigations, extensive laboratory studies were carried out through direct research in the AWTR laboratories at Cincinnati and through contract research by Radiation Applications Incorporated of Long Island City, New York, an organization having prior research and development experience in the separation and recovery of metal ions from solution and in isotope purification work. Other laboratory scale work was conducted by Esso Research and Engineering Company at Linden, New Jersey. To establish the feasibility of the foaming process for removing refractory materials from secondary effluents, both batch-foaming and continuous-feed-foaming techniques were employed.

In the continuous-feed-foaming studies, column-type foamers similar to that shown in Figure 7 were used. A gas sparger located at the bottom of the column produces fine bubbles that move upward through the liquid countercurrent to the flow of waste water. The downflowing water discharges through an opening at the bottom. Foam generated at the foam-liquid boundary near the top of the column is removed as it is forced upward owing to the drag of the airstream.

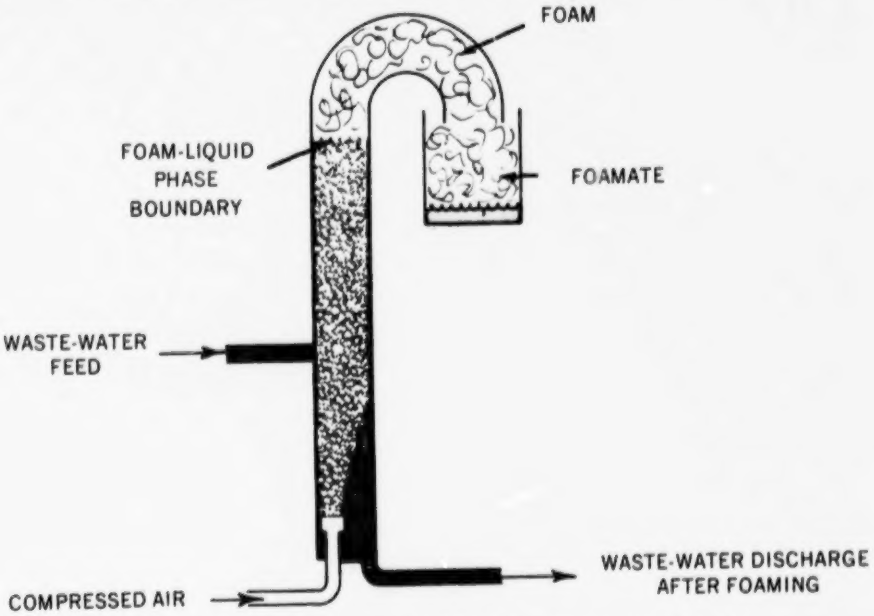

FOAM
FOAM-LIQUID PHASE BOUNDARY
FOAMATE
WASTE-WATER FEED
WASTE-WATER DISCHARGE AFTER FOAMING
COMPRESSED AIR

Figure 7. Column-type foamer used for laboratory evaluation of contaminant removal under continuous-flow conditions treating secondary sewage effluent.

Results of Laboratory Studies

Continuous-flow experiments using effluent from activated-sludge treatment plants have produced a number of significant findings summarized as follows (ABS content of the effluent before foaming ranged from 1. 1 to 4. 7 ppm and organic content measured by COD ranged from 85 to 195 ppm):

1. ABS concentrations between 2. 0 and 3. 2 ppm in secondary effluent are consistently reduced to between 0. 3 and 0. 5 ppm by using air-to-liquid flow rates (by volume) of 3. 5 to 7. 5:1 at residence times of 5 to 10 minutes (Figure 8).

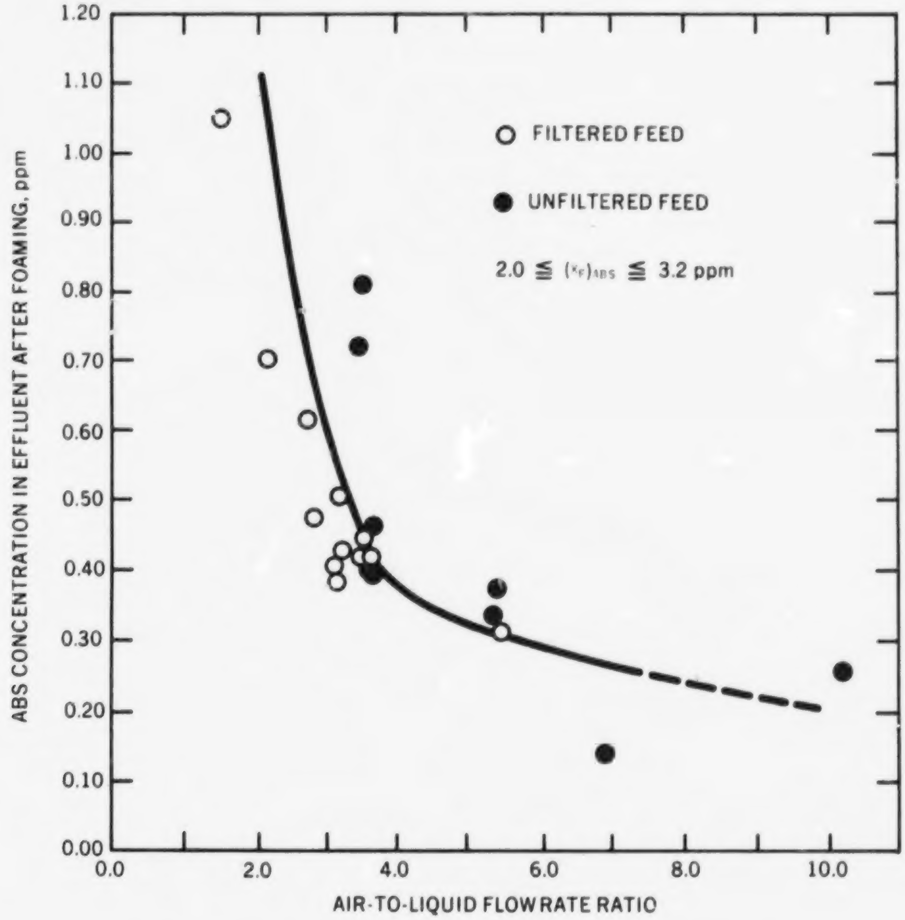


Figure 8. Foaming of secondary effluent in laboratory tests with a column-type foamer. Effect of air-to-liquid flow rate ratio on ABS concentration in foamed effluent.

2. Removal of total organics from secondary effluents has ranged from 10 to 45 percent; normal removal is 25 to 30 percent.

3. Preliminary studies showed that the addition of certain surface-active or nonsurface-active materials, or both, did not effectively increase contaminant removal during foaming; however, subsequent

tests with 5- to 10-ppm concentrations of specially selected cationic polyelectrolytes as additives have yielded organic removals of 65 to 75 percent from primary effluents and up to 65 percent from secondary effluents.

4. Definite synergisms exist among contaminants present in municipal waste waters, a factor that promotes improved removal efficiencies.

5. Evidently more COD is removed as surfactant concentration in the secondary effluent decreases; however, a minimum concentration of about 1 ppm surfactant is required to generate a stable foam to provide the physical means for removing COD-bearing materials.

6. Volume of the collapsed foam averaged about 1 percent of the feed volume.

7. Total dissolved solids and chloride ions have been found to be unaffected by the foaming process. An increase in pH upon foaming suggests that weakly acidic substances are removed.

8. ABS removal was not appreciably affected by filtering secondary effluent samples before foaming (Figures 8, 9, and 10)

9. Foam separation costs are projected to be less than 3 to 5 cents per 1,000 gallons exclusive of foamate disposal costs.

TROUGH-TYPE FOAMER

Although the column-type foamer (Figure 7) has proved highly effective in removing ABS to less than 1 ppm in laboratory scale units, use of this design for larger units appears questionable. A number of difficult design and operating problems are encountered in expanding the column-type design to a large-scale operation. For example, process requirements include (1) a residence time of 5 to 10 minutes in the column, (2) a downward liquid velocity less than the velocity of the rising air bubbles, and (3) production of comparatively small bubbles because of their greater surface area per volume of gas feed. To achieve these objectives, sizing of a foaming column to handle medium or large liquid volumes requires unusually large, horizontal projected areas. Some of the disadvantages in designing a scaled-up column-type foamer are: (1) achieving uniform distribution of feedwater over the top of a large-diameter column is complicated and expensive, (2) distributing inlet air over the entire bottom of the column presents similar difficulties, (3) discharging product water uniformly is difficult, and (4) collecting foams of low stability would require numerous small-diameter foam take-off ducts, which would create an expensive and complicated manifolding problem.

To use the foaming principle under conditions of such large volumes of flow as are encountered in treatment of municipal waste

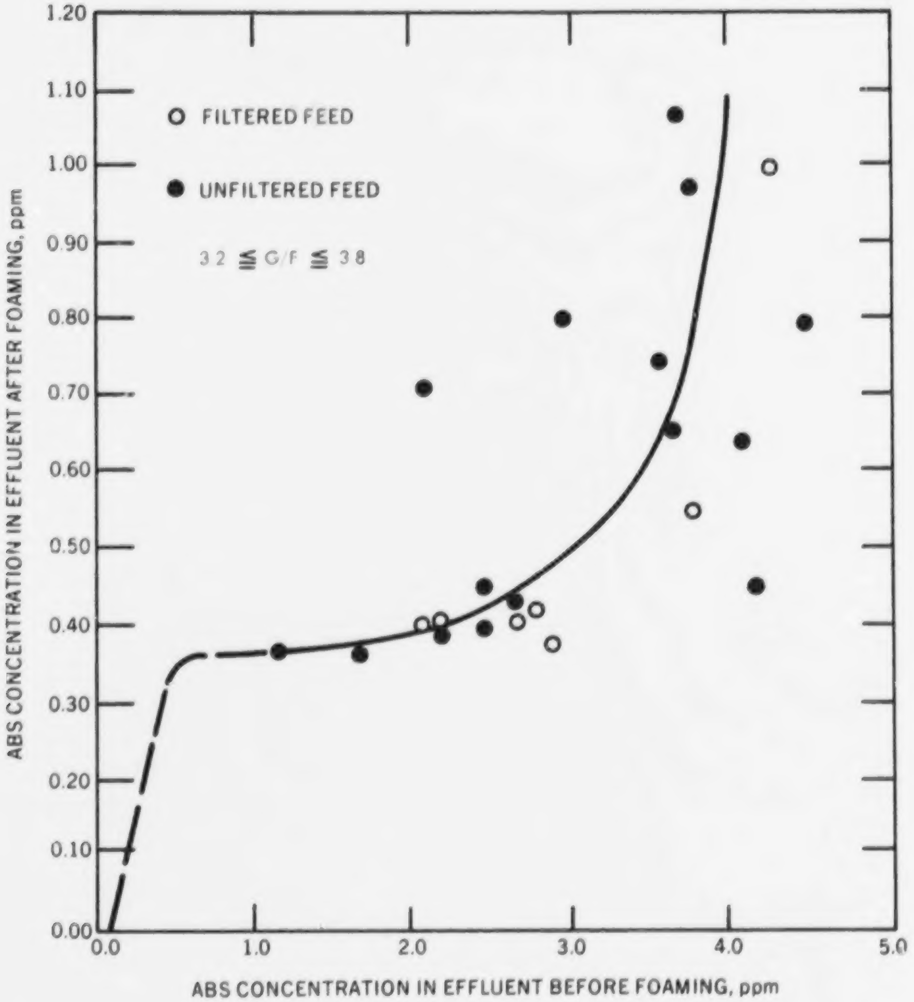


Figure 9. Foaming of secondary effluent in laboratory tests with column-type foamer: relationship between concentrations of ABS in secondary effluent before and after foaming.

streams, employment of trough-type foamers such as shown in Figure 11 has been necessary. In this design the waste stream flows horizontally through a covered trough. Fine air bubbles emerging from spargers placed along the bottom of the trough generate a foam at the foam-liquid boundary. The foam phase is maintained in the space between the liquid surface and the trough cover and transported to a discharge opening by the drag of the airstream as it leaves the enclosure. Present information indicates that removal efficiencies are lower in the trough-type foamer than in the column-type foamer, the best results attainable so far indicating that 1 to 2 ppm ABS is left in the effluent after treatment in the trough-type design.

Pilot Plant Studies

To evaluate design and operating variables of a large-volume, continuous-flow system, a 1/2-mgd trough-type foamer has been installed

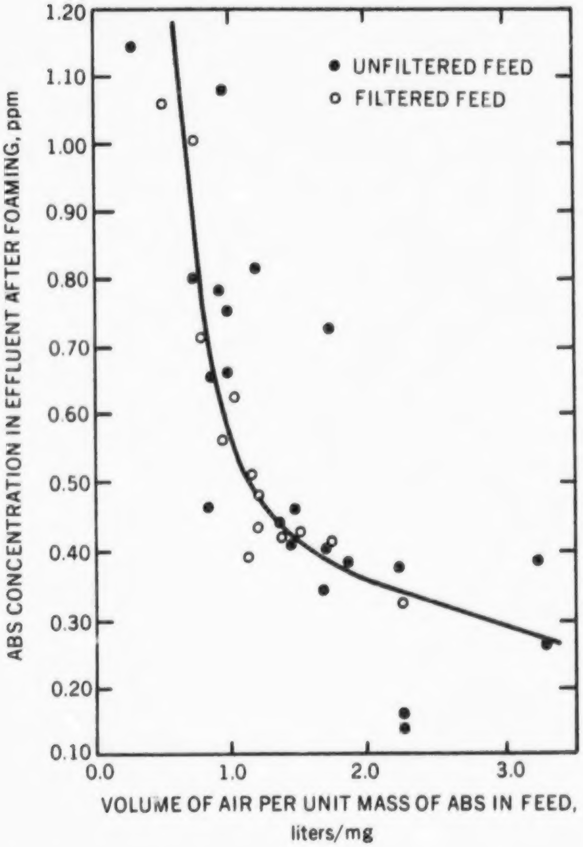
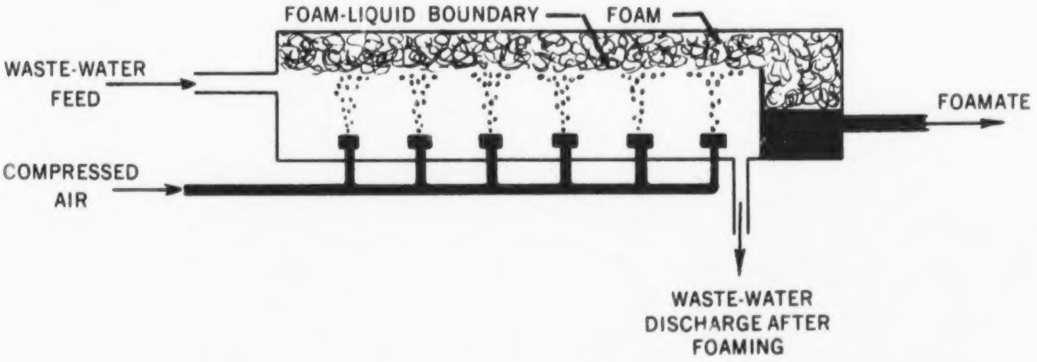


Figure 10. Foaming of secondary effluent in laboratory tests with column-type foamer: effect of air volume per unit mass of ABS on ABS removal.

at the municipal waste treatment plant in Pomona, California, under a joint research project with the Los Angeles County Sanitation District. Effectiveness of foam separation as a method of removing refractory contaminants from activated-sludge-treated effluent will be studied in this pilot plant, whose general arrangement is shown in Figure 12.



FOAM-LIQUID BOUNDARY
FOAM
WASTE-WATER FEED
FOAMATE
COMPRESSED AIR
WASTE-WATER DISCHARGE AFTER FOAMING

Figure 11. Trough-type foamer. ABS removal efficiency of this design is not as good as in column-type foamers. Residual ABS of secondary effluent after treatment in trough design is 1 to 2 ppm.

Among the variables involved are (1) liquid residence time, (2) air-to-liquid ratio, (3) liquid depth, (4) depth at which air is introduced, (5) foam residence or drain time, (6) air diffusion system used, (7) air use per unit cross-sectional area of tank, and (8) baffling arrangements in the tank to prevent longitudinal mixing and encourage counterflow of air and liquid.

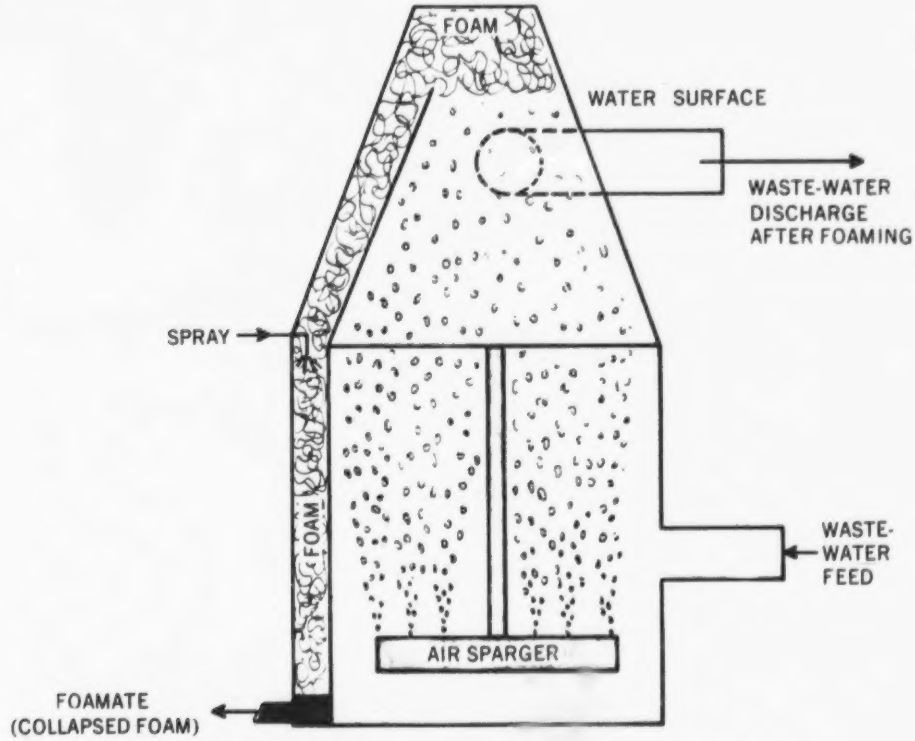


Figure 12. Cross section end view of ½ mgd foam separation pilot plant for treating effluent from an activated-sludge plant. The unit is 15 ft long x 3½ ft wide x 9 ft high. Water depth is approximately 6 ft.

The work to date has shown that foam separation can be accomplished in full-scale operation to achieve reductions of ABS in secondary effluents to 1.5 milligrams or less per liter and of COD by about 30 percent.

Investigations of the above factors to achieve optimization of the process are in progress. Initial results indicate that:

1. More ABS and COD are removed with air-to-liquid ratios up to 0.6 to 0.75 cubic foot of air per gallon of liquid than at greater ratios (see Figure 13).

2. Air introduced near the bottom of the tank removes more contaminants per unit volume of air than that introduced at lesser depths even though essentially complete vertical mixing takes place from currents set up by the rising air bubbles. This indicates that the collection of materials on the bubble interface during its travel to the sur-

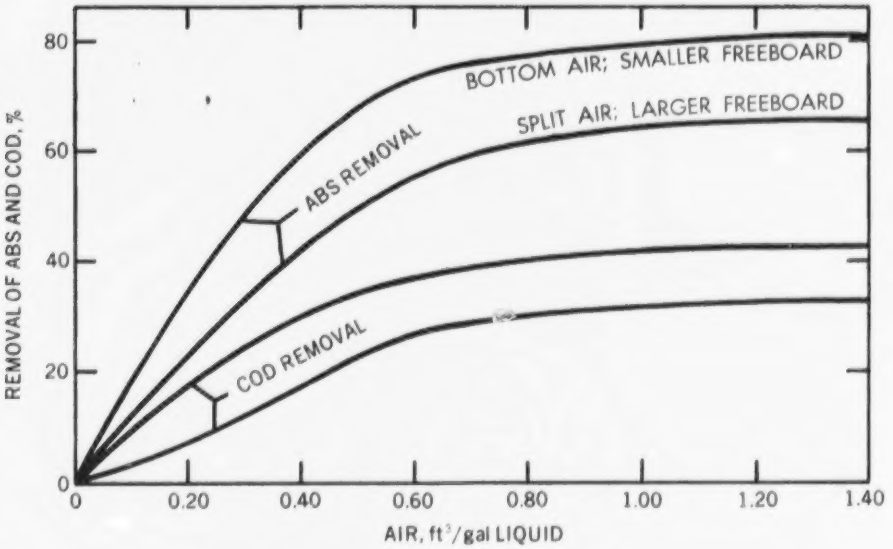


Figure 13. Foaming studies on ½ mgd pilot plant: effect of varying air-to-liquid ratios on ABS and COD removals from secondary effluent.

face influences significantly the amount of materials adsorbed when the bubble is formed. Liquid depth is, therefore, important.

3. The foam residence or drain time (controlled by the relative elevations of the liquid surface and foam overflow weir, and by the air rate) is a major factor in foamate volume. Larger foamate volumes achieve greater contaminant removals, but the practical limit for gain in removal at the expense of larger foamate volumes appears to be at conditions that limit foamate volume to less than 1 percent.

FOAM HARVESTING ON ACTIVATED-SLUDGE TANKS

In secondary waste treatment by the activated-sludge process, air is introduced into the liquid at the bottom of an aeration tank to provide an adequate supply of oxygen for the biological processes occurring. From the standpoint of air-liquid contacting, the process is not unlike the foam separation process itself. In fact, the formation of foam on activated-sludge treatment tanks due to the extensive aeration involved is a significant problem that has required considerable study and expense to resolve. The commonest solution has been to direct water sprays onto the foam causing it to collapse back into the main body of liquid.

A logical assumption is that removal of the foam from activated-sludge tanks would have the same general effect in reducing refractory organic contaminants as has been observed in foam separation studies on secondary effluents. In other words, by removing the foam already produced during secondary treatment, it is conceivable that refractory organics could be substantially reduced without further foaming in a special tertiary foam separation unit.

To evaluate the practicability of this technique, a study was undertaken with the objective of collecting the foam produced on the surface of an activated-sludge aeration tank and evaluating the efficiency of removal of refractory contaminants by such an approach. For this study a foam-harvesting system was devised consisting of a perforated pipe floated on the surface of the water near the wall of the tank at which foam accumulated. Foam was drawn into the tube by a suction system, which included an exhaust blower connected to the perforated pipe. The foam collapsed inside the tube and drained to a sump from which it was pumped out for final disposal (see Figure 14).

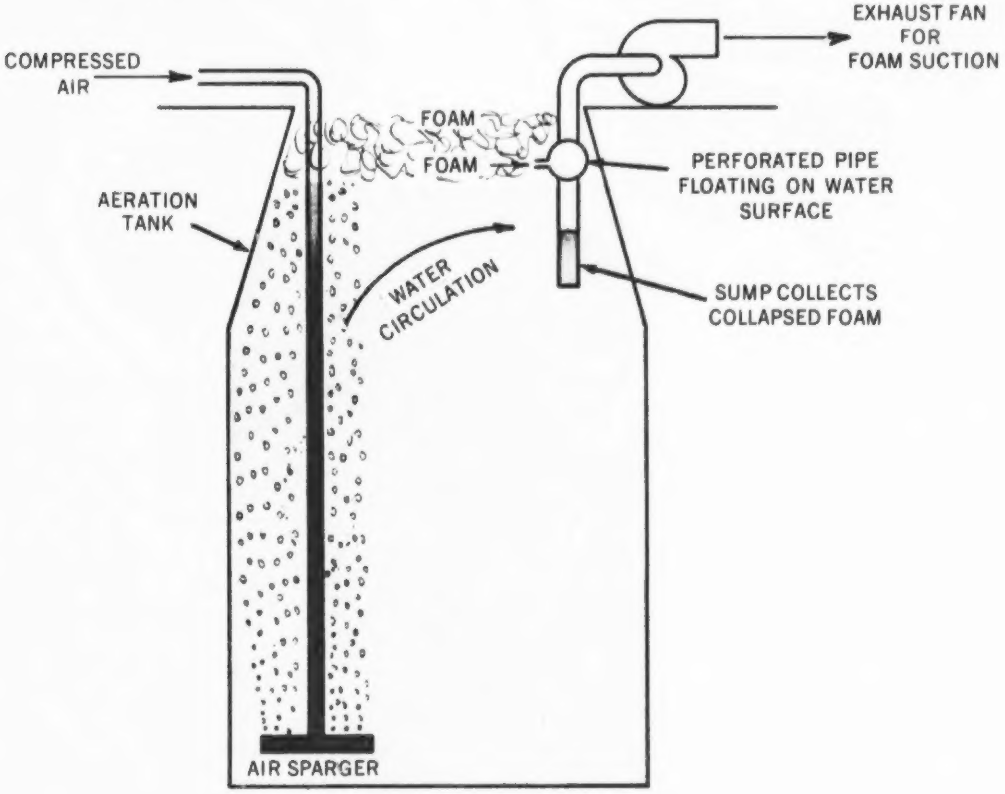

EXHAUST FAN FOR FOAM SUCTION
COMPRESSED AIR
FOAM
FOAM
PERFORATED PIPE FLOATING ON WATER SURFACE
AERATION TANK
WATER CIRCULATION
SUMP COLLECTS COLLAPSED FOAM
AIR SPARGER

Figure 14. Foam harvesting on activated-sludge aeration tank – proposed as a method for reducing refractory organics in secondary effluent. Although foam produced was successfully collected, the activated-sludge aeration tanks could not be operated so as to produce foam continuously.

The foam collection system was developed to the point of successfully removing the foam as it was generated and transported across the water surface by the movement of water in the tank. In operating the prototype collection system, which extended over a short length of a 330-foot-long aeration tank, it soon became apparent that foam generation does not occur as uniformly and consistently during the day-to-day operation of an activated-sludge tank as was thought. The plant at which the study was made had a past record of serious foaming on its aeration tanks; but during this study, when the formation of foam was observed continuously on a 24-hour basis over an extended period, it was seen that foam is produced only intermittently.

Efforts were made to produce foam intentionally by adjusting the suspended-solids concentration in the activated-sludge tanks, but the efforts were unsuccessful insofar as continuous foam formation was concerned. Half a dozen other treatment plants in the vicinity with past records of foam problems were surveyed for their foam production, but in each case, continuous and detailed observations revealed that foam was not produced as continuously or as voluminously as predicted.

Because of the inconsistent production of foam, the suitability of a foam-harvesting system for achieving any appreciable degree of contaminant removal is considered questionable. For this reason the study has been discontinued.

Electrodialysis

ELECTRODIALYSIS PRINCIPLE

When an electric potential is impressed across a cell containing mineralized water, positively charged ions (cations) migrate to the negative electrode, and negatively charged ions (anions) migrate to the positive electrode. If cation- and anion-permeable membranes are placed alternately between the electrodes, ions will concentrate in alternate compartments and become more dilute in the intervening compartments (see Figure 15). This process is called electrodialysis. If the apparatus is arranged so that concentrated and diluted streams flow continuously, a device useful for large-scale demineralization of water results. Only partial demineralization by this method is practical, however, because electrical power requirements become excessive if the ion concentration is reduced too far. Fortunately, power consumption remains reasonable at the mineral ion concentrations occurring in drinking water. Since the electrodialysis phenomenon is specific for ions, application of the process is limited to removal of soluble ionized contaminants.

For treatment of brackish water, commercial application of electrodialysis has already been found successful (see Figure 16). A unit operating at Buckeye, Arizona, has a capacity of 650, 000 gpd and provides the potable water supply for that community. Although the present treatment cost for this plant is about 30 to 35 cents per 1, 000 gallons on a full-load basis, this figure would undoubtedly be lower for larger plants. Since municipal waste waters have mineral compositions similar to those of many brackish waters, it was assumed, prior to initiation of research on this process, that partial demineralization of waste water by electrodialysis would be feasible. Municipal waste waters do, however, contain both soluble and collodial organic matter whereas organics are not normally present in brackish waters. Some of this organic matter in waste waters, including much of the synthetic detergent, is ionic, but a major fraction is un-ionized. The potentially deleterious effects of this organic conglomerate are practically unknown.

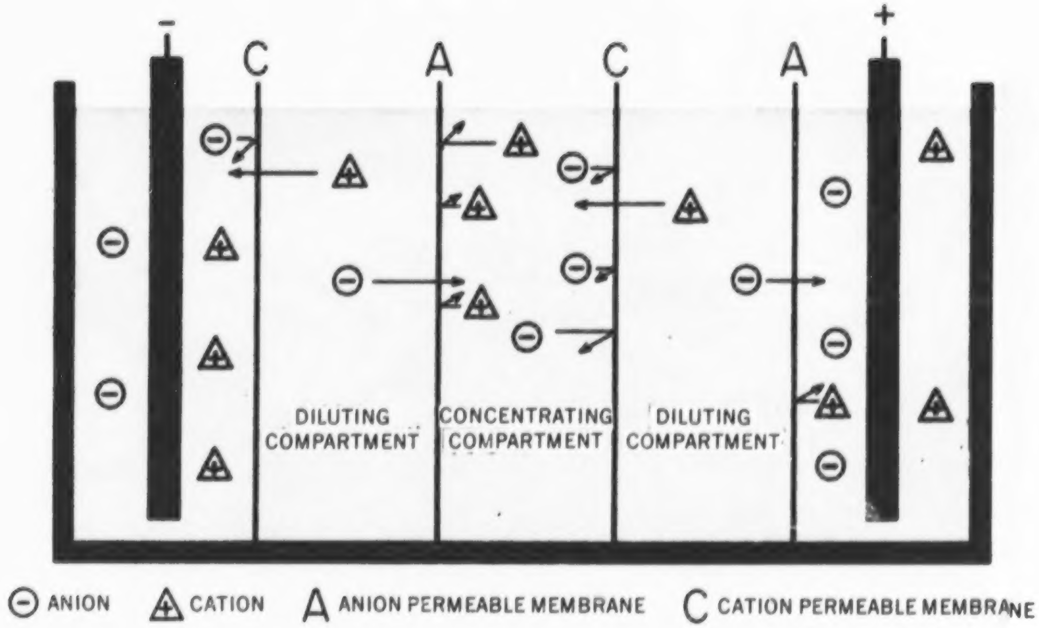

-
C
A
C
A
+
DILUTING COMPARTMENT
CONCENTRATING COMPARTMENT
DILUTING COMPARTMENT
ANION
CATION
A ANION PERMEABLE MEMBRANE
C CATION PERMEABLE MEMBRANE

Figure 15. Principle of electrodialysis. Positive ions in the diluting compartment are attracted to the negative electrode and pass through the cation-permeable membrane but cannot pass through the anion-permeable membrane. They thus become trapped in the concentrating compartment. Similarly, negative ions attracted to the positive electrode are removed from the diluting compartment as they pass through the anion-permeable membrane to be trapped in the concentrating compartment. This process results in the demineralization of water in the diluting compartments.

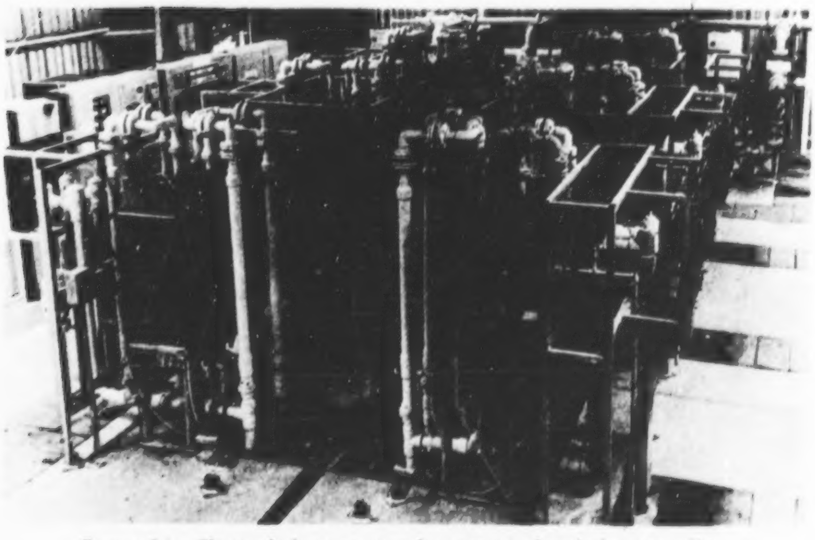


Figure 16. Electrodialysis system for treating brackish water. This installation is being used to convert brackish well water to potable water at Buckeye, Arizona. During treatment the mineral content of the water is reduced from about 2,000 to 500 ppm. The capacity of the system is 650,000 gpd.

STUDY PROJECTS

To study the effects of organic materials on operating efficiency of the electrodialysis process, the Program negotiated contracts with Ionics, Incorporated, and the Polytechnic Institute of Brooklyn. The specific objectives of these projects were to establish whether or not organic ions could be removed by electrodialysis and whether or not they would cause fouling of the membranes. Initial investigations were made with synthetic waste waters containing ABS as the only organic constituent. Results of the first study demonstrated that (1) electrodialysis is not a practical method of removing ABS from water, and (2) the ABS anion hinders good operation by fouling the anion-permeable membranes. Although it was possible to make very porous membranes that allowed organic ions to pass, they also allowed a considerable amount of water to pass into the concentrating compartments. The conclusion was that soluble organic contaminants should be removed before electrodialysis to achieve efficient long-term operation.

In a further study carried out by Ionics, Incorporated, electrodialysis was evaluated in a series of tests with municipal secondary effluent. Two small electrodialysis stacks (Figure 17) were operated at a feed rate of about 120 milliliters per minute for a total run time of 1,500 hours. The waste stream fed to one stack was first passed through a column of activated carbon for removal of suspended and soluble organic matter; the feed to the other stack was filtered to remove suspended solids of greater than 10-micron size, but soluble organics were allowed to remain.

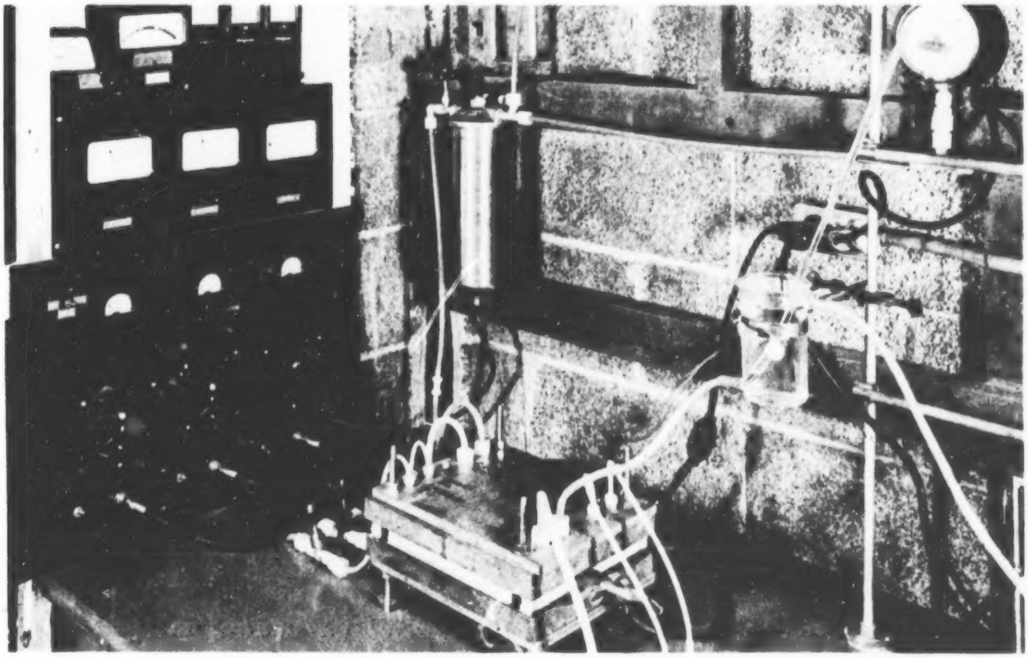


Figure 17. Laboratory scale electrodialysis stack. About half of the mineral content of waste water can be removed by passing the water through this stack.

RESULTS

Stack electrical resistance was higher on the unit receiving filtered waste water than on the unit receiving carbon-treated waste water. This higher resistance was shown to be due primarily to a decrease in conductivity of the anion membranes because of clogging by ABS and other organic anions. By rinsing the anion membranes with a hydrochloric acid-acetone mixture, it was possible to remove much of the accumulated organic matter and thereby decrease the resistance from five times that of new membranes to twice that of new membranes. This evidence substantiates the desirability of removing high-molecular-weight organic ions from waste water before electrodialysis.

Significant amounts of all common mineral ions were removed from the waste water studied. Although the degree of removal of particular ion species varied somewhat with operating conditions, no correlation to predict selectivity was developed. The process is, very generally, nonselective.

One phase of the study involved a series of tests to determine the extent to which concentration of salts in the concentrating compartments could be increased without precipitating less soluble materials upon the membranes (Figure 18). This is important in establishing the volume of concentrated waste brine for which ultimate disposal or further treatment will be required. This evaluation was made by recirculating liquid from the concentrating compartments and back to them after bleeding off a small fraction and adding a small fraction of fresh waste-water feed. Attainment of a concentrate volume of less than 10 percent of the feed volume was found to be possible provided pH is controlled by sulfuric acid to prevent calcium carbonate scale. With hydrochloric acid it was possible to decrease the concentrate volume to less than 1 percent of the feed volume.

Results from the Ionics laboratory study led to the conclusion that electrodialysis is a technically feasible method of demineralizing municipal waste water to the extent required for most uses. It is now necessary to obtain operating data and cost information on larger scale equipment. Present plans are to install and operate an electrodialysis stack with a product capacity of 70, 000 gpd. The unit will be made as portable as possible to facilitate operating at other sites later. The results from this pilot stack are expected to provide a sound basis for making realistic estimates of the costs and operational requirements for full-size plants. Present information indicates that total cost of treatment for a 10-mgd plant should be 20 cents or less per 1, 000 gallons exclusive of feed pretreatment and brine disposal.

Reverse Osmosis

OSMOSIS PRINCIPLE

A natural phenomenon known as osmosis occurs when solutions of two different concentrations are separated by a semipermeable mem-

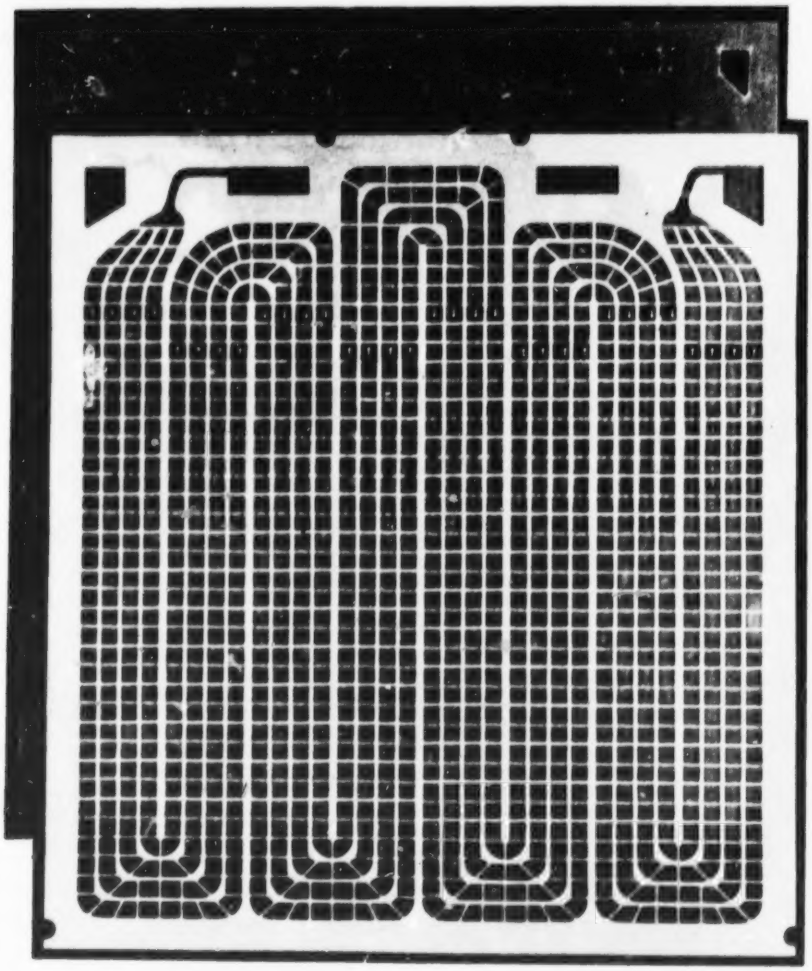


Figure 18. Electrodialysis membrane spacer. To obtain close, uniform spacing of two electrodialysis membranes and still prevent contact, a thin sheet of plastic is placed between them. Openings are provided in the plastic sheet to allow water flow across the membranes. In spacer designs such as this one, the water is forced to flow over a long, tortuous path. This insures that water moves over the entire membrane surface. Plastic strips across the flow path, thinner than the rest of the spacer, promote turbulence in the water and increase the removal capability of electrodialysis stacks.

brane such as cellophane. With such an arrangement, water tends to pass through the membrane from the more dilute side to the more concentrated side and produce concentration equilibrium on both sides of the membrane. The ideal osmotic membrane permits passage of water molecules but prevents passage of dissolved materials. The driving force that impels this flow through the membrane is related to the osmotic pressure of the system, and this pressure is proportional to the difference in concentration between the two solutions. The principle is illustrated in Figure 19A. If the liquid on the more concentrated side is allowed to rise in a standpipe as water passes through the membrane, as shown in Figure 19B, the hydrostatic pressure on the right side of the membrane gradually increases until it finally equals the osmotic pressure. At this point, flow through the membrane ceases. If, then, we intentionally increase the pressure on the more concentrated (right) side of the membrane, as shown in Figure 19C, the flow of water through the membrane reverses, that is, water moves from the more concentrated compartment to the less concentrated compartment. This method of purifying water is popularly called reverse osmosis, though the mechanism of water transfer may not be the same as in normal osmosis.

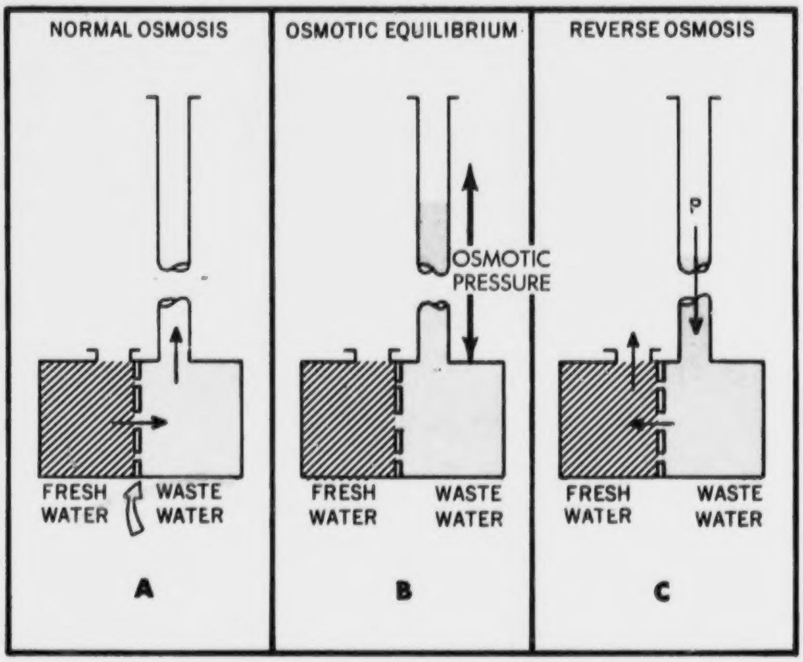


Figure 19. Schematic representation of principles involved in normal osmosis and reverse osmosis.

The properties of a membrane that permit water molecules to pass through but impede the flow of contaminant molecules are not clearly understood. It is believed to be not simply a molecular filtering action, even though individual water molecules are smaller than most of the contaminant molecules of concern. Some scientists believe that water passes through the membrane by the progressive formation of hydrates. Only H_2O molecules can form hydrates, which accounts for the passage of only pure water.

STUDY PROJECTS

Because reverse osmosis has come into prominence only recently, there are no commercial applications of it at present. In addition to the Public Health Service's AWTR Program, other research programs on reverse osmosis are being sponsored by the Department of Interior's Office of Saline Water for demineralizing sea water and brackish water, and by the National Aeronautics and Space Administration and the Air Force for the recovery of water from urine.

The Aerojet-General Corporation, of Azusa, California, has had considerable experience in designing membranes for use with different types of solutions and in developing equipment suitable for employing reverse osmosis as a continuous-flow water treatment process. Upon learning of the objectives of the AWTR Program, Aerojet-General undertook some preliminary experiments in their laboratories to establish the general suitability of reverse-osmosis membranes and equipment for the treatment of waste-type solutions. At that time, it was not known what problems would arise from the presence of surface-active materials, organic solutes, or bacteria in waste waters. Their exploratory studies demonstrated that all these materials can be effectively removed by the process. For example, a solution containing 2,500 ppm sodium chloride and 115 ppm ABS yielded a product containing 160 ppm sodium chloride and only 3 ppm ABS. In this test, treatment was accomplished at a rate of 34 gpd per square foot of membrane surface.

Based on these encouraging results, a contract was negotiated with the Aerojet-General Corporation to estimate the technical and economic feasibility of using reverse osmosis for renovation of municipal waste waters. It called for evaluation of the contaminant removal efficiencies of standard and special membranes installed in laboratory scale reverse-osmosis units operated at 750 and 1,500 psi. The evaluations were made on filtered municipal secondary effluent.

The experimental equipment included two reverse-osmosis cells, each capable of accommodating 0.5 square foot of membrane. The cell housings were constructed of a glass-cloth epoxy resin to eliminate corrosion problems. Figure 20 shows one of these cells unassembled; Figure 21 shows two cells set up in series and ready for operation. The complete reverse-osmosis system including the feed tank and pump is illustrated in Figure 22.

The membranes tested varied in "tightness" and had varying nominal-flow capacities ranging from 10 to 60 gallons per square foot per day. The test procedure for evaluating rate of flow through different membranes involved continuous operation at 750 or 1,500 psi for 5- to 6-hour periods. In most of the tests, the concentrated liquor from the waste side of the reverse-osmosis cells was returned to the feed tank, which produced a continual increase of dissolved-solids concentration in the feed water, which eventually amounted to a 5- to 10-fold increase. Early in the study, maintenance of the pH of the waste water at 5.5 or below by adding sulfuric acid ahead of the cells was found necessary. Without this acid treatment, a deposition of acid-soluble scale formed on the membranes causing as much as a 70 percent drop in waterflow (flux rate) through the membrane after only 3 hours of operation. Even at the low pH there was, in all cases, a rapid decrease in flux rate for the first 2 to 3 hours, and thereafter the decrease was more gradual but still continued throughout the test period. At the end of the test period, the decreases in flux rates ranged from 45 to 68 percent of the initial values. This inability to maintain suitable flux rates for any extended period of time raises questions about the economic feasibility of this process in comparison with other effective treatment processes.

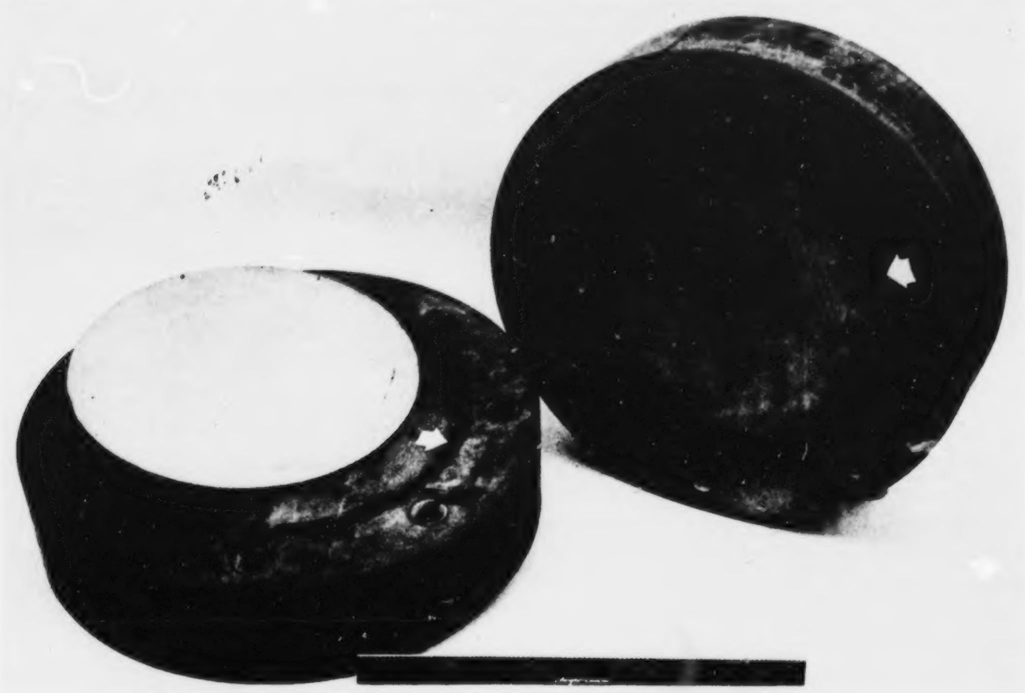


Figure 20. Glass-cloth epoxy reverse-osmosis cell (unassembled) used for waste-water renovation experiments. Also shown is the glass-cloth epoxy backup plate that supports the membrane. The arrows point to the O-ring seal.

RESULTS

Although the final flow rates achieved during the 6-hour tests were considered unsatisfactory, there is some evidence to indicate that significantly higher flows can be obtained by modifying the operating procedures. This expectation is based on the results of a single test in which (1) the organic content of the waste water was removed by activated-carbon treatment ahead of the reverse-osmosis cell, and (2) waste concentrate from the reverse-osmosis cell was not returned to the feed tank, so that the test involved only a single pass of the liquid through the cell. Under these changed conditions, the decrease in flux rate was significantly retarded.

Results of the 6-hour tests conducted at a pressure of 1,500 psi were much the same as those produced by the tests at 750 psi. Apparently, then, there is no advantage in using the higher pressure. The reason for this is not understood at this time though it may be simply a result of membrane compression.

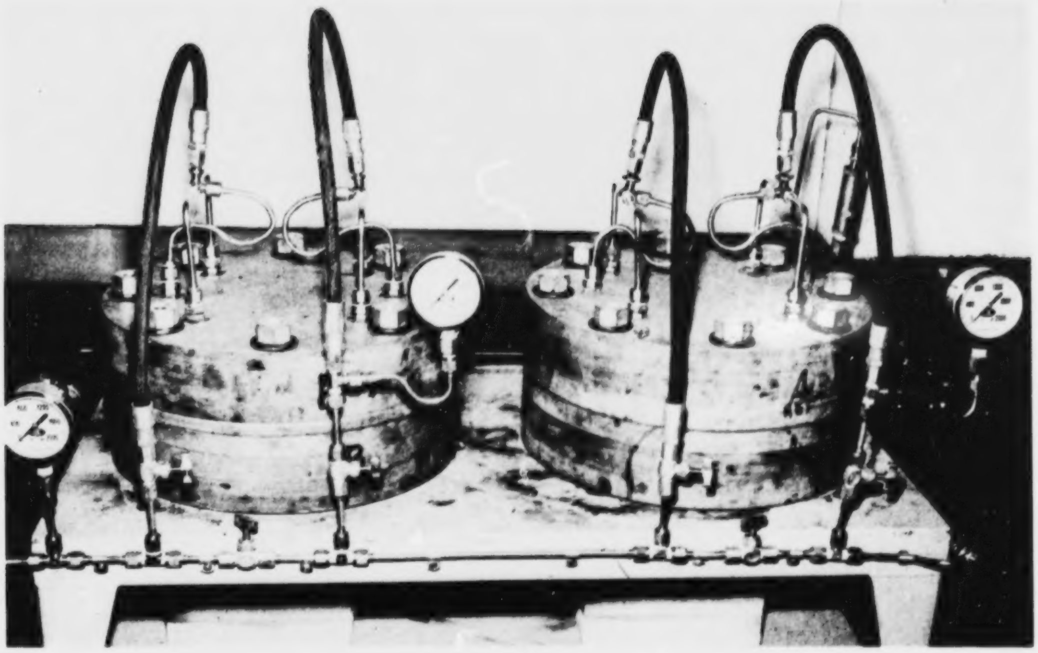


Figure 21. Experimental reverse-osmosis cells arranged for series flow during tests to purify municipal waste water.

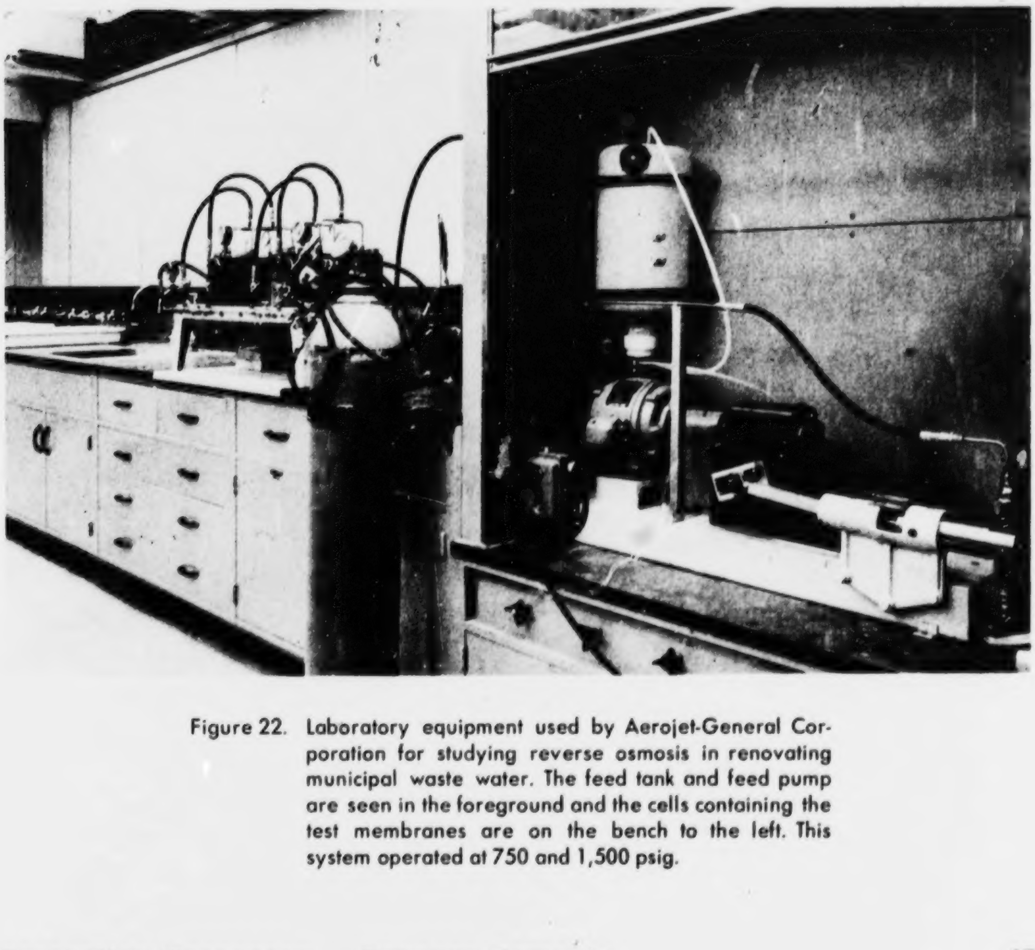


Figure 22. Laboratory equipment used by Aerojet-General Corporation for studying reverse osmosis in renovating municipal waste water. The feed tank and feed pump are seen in the foreground and the cells containing the test membranes are on the bench to the left. This system operated at 750 and 1,500 psig.

Reverse osmosis proved very effective in removing contaminants from waste water under all conditions tested. Typical of the high quality of the product water are the analyses of two tests reported in Table 2 showing up to 97 and 98 percent reductions in TDS, ABS, and COD. In another test, average product concentrations (in ppm), after 88 percent of the feed had been passed through the membrane, were TDS 126, ABS 0.3, and COD 12.

Table 2. COMPOSITION OF WATER PRODUCED BY TREATING MUNICIPAL WASTE WATER BY THE REVERSE-OSMOSIS PROCESS

Component	Feed water (typical), ppm	Product Test 1, ppm	Product Test 2, ppm
TDS	550	15	28
ABS	4.5	0.1	0.1
COD	95	2	6.0
pH	5[a]	6.3	5.5
Cations			
Na^+	85	4.6	6.1
K^{++}	40	4.9	2.7
NH_4^+	25	0	3.9
Ca^{++}	125	0	2.6
Mg^{++}	50	0.7	0
Fe^{++}	N.D.[b]	0	0
Anions			
Cl^-	65	20.3	22.1
NO_3^-	2	0	0
HCO_3^-	260	8.1	3.5
$CO_3^=$	0	0	0
$SO_4^=$	200	1.7	3.3
$SiO_3^=$	30	2.9	2.9
$PO_4^=$ (total)	25	0	0

[a] pH adjusted during test.

[b] N.D. = not determined.

Flow through reverse-osmosis membranes decreases if physical or chemical fouling occurs; membranes may also be affected by biological attack. That a membrane suspended in flowing secondary effluent for 9 days suffered a 24 percent decrease in flux rate is evidence of possible trouble. Clearly, these are areas requiring much study before final conclusions may be drawn regarding the suitability of this process for AWT applications.

Although many problems remain, preliminary studies indicate that reverse osmosis has promise as a possible method for complete renovation of municipal waste waters. The quality of water produced is especially noteworthy and compares favorably with the product from distillation equipment.

Extended laboratory studies are needed to evaluate this process further and supply answers to the many questions raised by the first series of tests. It will be necessary, for example, to determine how long satisfactory flux rates can be maintained with a continuous feed of unconcentrated waste water. Extensive information is required on membrane life, particularly under conditions of actual operation. The extent and type of pretreatment of feed water necessary must be determined. Inasmuch as 750 psi was the lowest operating pressure used in these tests, further work is necessary to establish the minimum practicable operating pressure and the effect lower pressure operation would have on the economics of the process.

Distillation

DISTILLATION PRINCIPLE

Distillation has long been known as a process for producing "pure" water. It is capable of removing both organic and inorganic dissolved contaminants with relatively high efficiency; suspended solids are eliminated and even microorganisms are destroyed by the above-boiling temperatures generally employed. Volatile impurities in the feed pass over into the distillate, but several "polishing" techniques are available to eliminate this problem.

Compared with the "organic only" or "inorganic only" removal processes, distillation remains a relatively expensive process even though much recent work in the desalinization field has been aimed at decreasing costs. The prospects of lower cost nuclear energy or combination water renovation-power plants might improve the economics significantly in the future. The only reason for even considering the "total removal" processes, exemplified by distillation, however, is that they produce a product water that is "too good"—water that may be blended with another stream to reduce greatly the effective cost of the total removal process.

For distillation to be economically practical, the latent heat of evaporation must be re-used many times. Three types of systems are commonly used to achieve this heat economy. In the first type (Figure 23), the multiple-effect evaporator, each effect is maintained at a slightly lower pressure and, hence, a lower temperature than the preceding one. This allows the steam produced in one effect to be used as the heating medium for the next. The result is that for each pound of steam supplied to the first effect, there is produced a number of pounds of product water approximately equal to the number of effects.

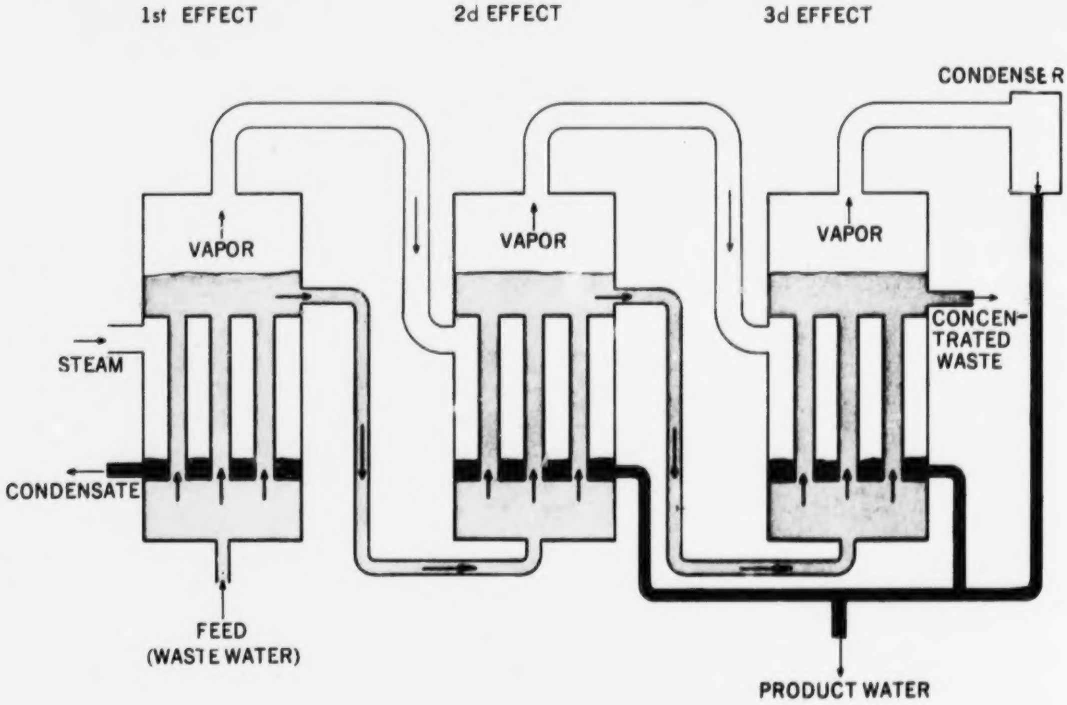

1st EFFECT
2d EFFECT
3d EFFECT
CONDENSER
VAPOR
VAPOR
VAPOR
STEAM
CONCENTRATED WASTE
CONDENSATE
FEED (WASTE WATER)
PRODUCT WATER

Figure 23. Schematic arrangement of multiple-effect evaporator.

The second type, known as the multi-stage flash still (Figure 24), is constructed so that water flash evaporates in a number of stages at successively lower temperatures. The heat of condensation is used to preheat the feed. It is necessary to add only a small amount of heat to the hot feed to raise its temperature the few degrees needed so that it is hot enough for flashing in the first stage. The heat economy depends on the number of stages and on the amount of temperature boost given to the preheated feed.

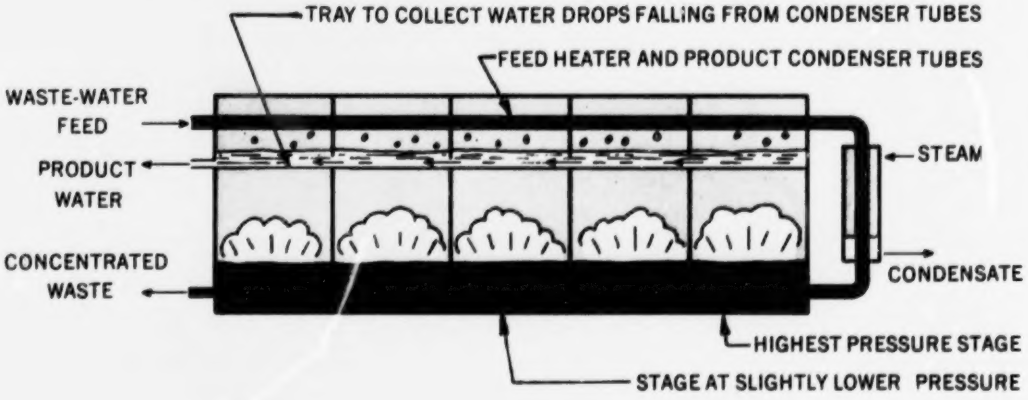

TRAY TO COLLECT WATER DROPS FALLING FROM CONDENSER TUBES
FEED HEATER AND PRODUCT CONDENSER TUBES
WASTE-WATER FEED
PRODUCT WATER
STEAM
CONCENTRATED WASTE
CONDENSATE
HIGHEST PRESSURE STAGE
STAGE AT SLIGHTLY LOWER PRESSURE

Figure 24. Schematic arrangement of multistage-flash evaporator.

Heat re-use is accomplished in the third type, the vapor compression still (Figure 25), by raising the temperature of the steam produced, through mechanical compression, to a temperature high enough that its own heat of condensation can be used to evaporate more water. Although no heat energy is required after startup, mechanical energy is necessary to compress the water vapor.

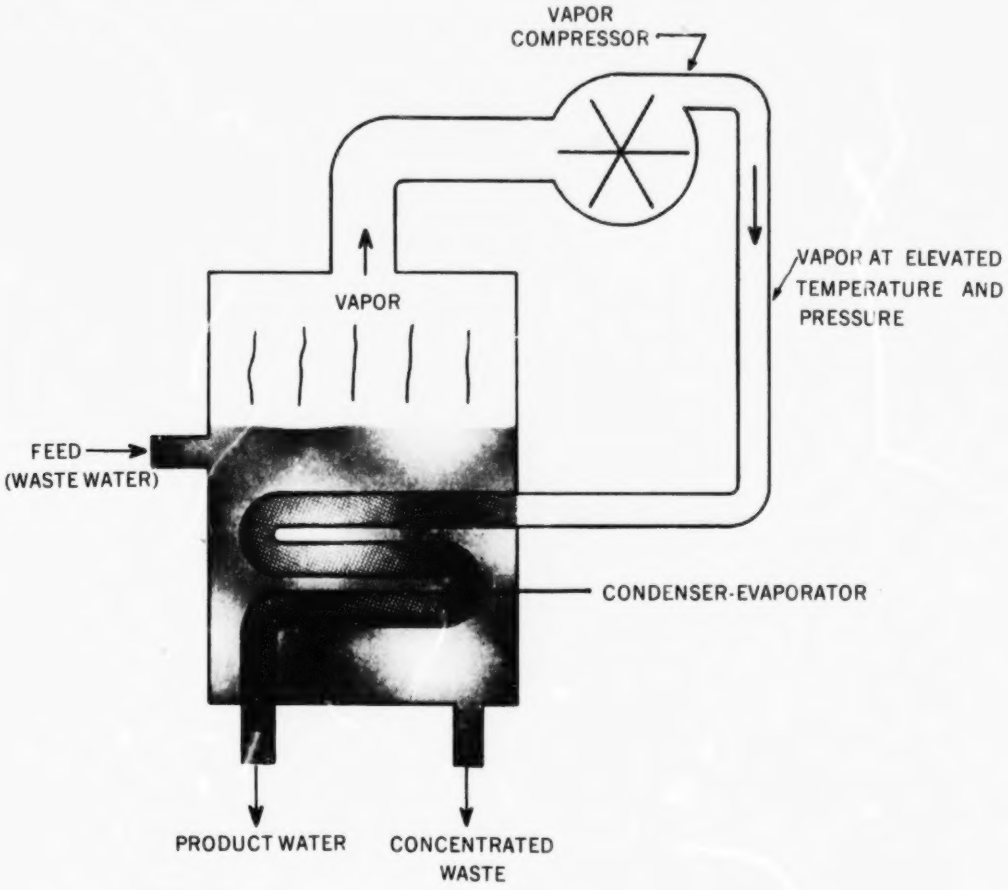


Figure 25. Vapor compression distillation.

STUDY PROJECTS

As the first step in evaluating distillation as a possible method of treating waste waters, opinions were obtained from four distillation experts concerning the applicability of the process to advanced waste treatment. The conclusion was that distillation of waste water would be generally similar to distillation of sea water but that a number of significant differences would exist. These relate to either the large difference in feed concentration or to the difference in type of contaminants present. While it was anticipated that waste-water distillation might have some practical and cost advantage over sea-water distillation owing to lesser dissolved solids content, it was also recognized that a waste-water feed has disadvantages owing to the presence of suspended solids and volatile materials. A rather detailed study by

Dr. J. A. Gerster of the University of Delaware indicated that, owing to the smaller concentration of scale-forming materials, the top distilling temperature for waste water might be considerably higher than that for sea water. This could lead to lower distilling costs. Dr. Gerster concluded, however, that possible additional feed pretreatment costs and ultimate disposal of concentrated wastes would probably bring the total cost of the product water to about the same level as for that produced from distilling sea water. His analysis indicated that multi-stage flash evaporators or multiple-effect evaporators appear to be the most appropriate types for this application.

Further investigation of distillation involved a paper study by W. L. Badger and Associates to determine the fraction of total waste-water flow that would have to be distilled to produce completely renovated water if renovated water constituted the total water supply and, for simplification, neither addition nor consumptive use of water occurred at any point in the system. Figure 26 shows the type of theoretical system considered. The assumption was that distillation would remove all contaminants from the distilled fraction and that some other process, for example, adsorption, would remove all organic material from the fraction not distilled. A major goal for a successful water renovation technology, incidentally, is that essentially all organic material be removed. Inorganic removal, on the other hand, should definitely not be complete since some degree of mineralization in a water supply is desirable.

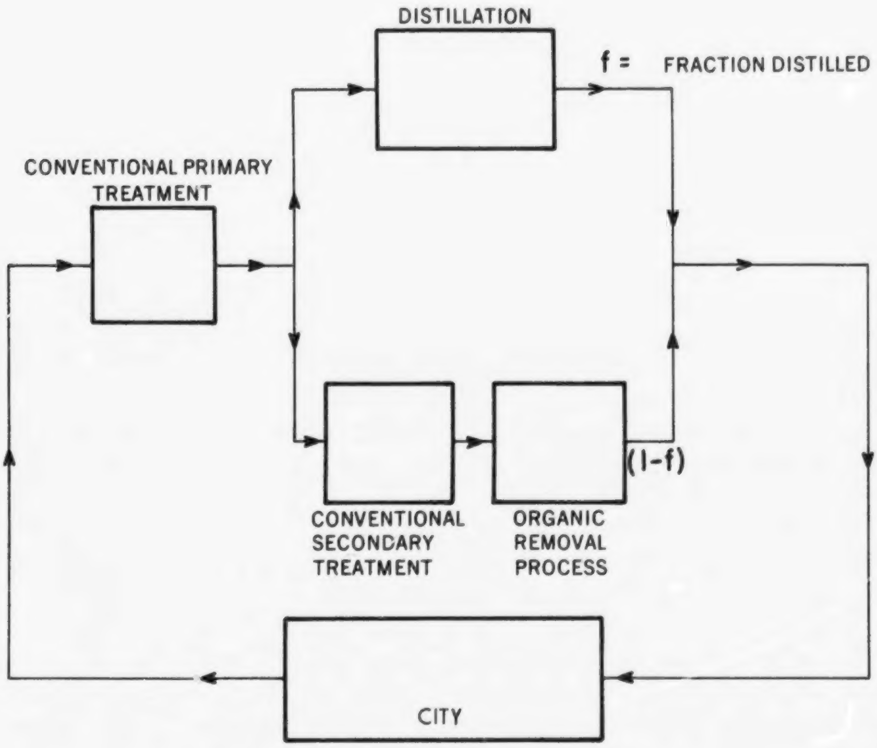


Figure 26. Simplified complete recycle system.

To establish the fraction required to be distilled for the recycle system shown in Figure 26, the study used data assembled by the AWTR Program on concentrations of inorganic ions in the tapwater and secondary effluent reported from 22 cities throughout the United States. From these data, the increments of individual ions added during water use were estimated. The quality of the product water to result from blending of the distilled and nondistilled fractions (Figure 26) was set at pre-established levels of inorganic ion content. The fraction to be distilled for each of the communities was then calculated on the assumption that inorganic ion content of the product would not be permitted to exceed the established concentration limits. Results indicated that the distillation requirements to meet these conditions ranged from 24 to 68 percent of the total waste flow.

Since organic removal treatment including any necessary pretreatment should be considerably cheaper than distillation, the parallel-flow treatment system should result in a significantly lower total product cost. Unfortunately, this "blending" technique cannot be applied in the conversion of sea water because of the much larger feed concentration. It is conceivable, however, that meaningful economics in sea-water conversion could be accomplished through blending a sea-water distillate, for example, with an organic-free but still-mineralized waste water.

To save on fuel costs, it is desirable to operate thermal stills at as high a temperature as possible. The highest temperature at which distillation can be carried out is most often limited by the concentration of scale-forming materials (i.e., Ca^{++}, Mg^{++}, HCO_3^-, $SO_4^=$) in the water. These materials will form hard scales on the heat transfer surfaces of the still and result in inefficient operation. In the waste waters analyzed by Badger Associates the range of maximum distillation temperature was predicted to be between 250° F and 400° F depending on feed composition and descaling method used. Owing to the presence of appreciable amounts of phosphates in waste water, it is possible that some of the calcium present will be removed as a nonscaling soft sludge of calcium phosphate, which would decrease the calcium sulfate scaling problem.

Experiments undertaken as part of Badger Associates' study consisted of continuous-flow boiling runs made at temperatures up to 250° F at the Ann Arbor, Michigan, waste-water treatment plant. The equipment used was a single steam-jacketed, rising-film, vertical evaporator tube. The single effort to distill primary effluent resulted in physical plugging of the tube with suspended matter. This particular primary effluent had rather large amounts of suspended matter at the time, which caused more serious plugging than would normally be expected. No organic fouling was observed on tests made with secondary effluent, but scaling due to calcium carbonate did occur. Acidification of the feed to a pH of 6 or less readily eliminated the scaling, and, most importantly, the presence of dissolved and colloidal organics did not complicate the situation. Calcium sulfate scaling was not encountered up to the 250° F maximum temperature employed. Corrosion of brass in the system, probably due to ammonia, was appreciable. The stainless steel boiling tube was not affected by corrosion during these runs.

A current contract with the American Machine & Foundry Company involves an investigation of multi-stage flash evaporation on a small pilot scale. Secondary effluent and possibly primary effluent will be used in the investigation. The equipment will consist of an 8-stage flash unit of approximately 1,000 gpd capacity. Factors that will be studied include scaling, corrosion, and product quality. Results from preliminary tests with only a single-stage unit (Figure 27) operating on primary effluent verify that good inorganic removal is achieved. There is, however, a carryover of volatile, odorous organics into the distillate that will have to be removed by a polishing treatment before the product water can be considered of acceptable quality.

Although only relatively limited experiments have been done to evaluate the feasibility of distilling waste waters, this process is pres-

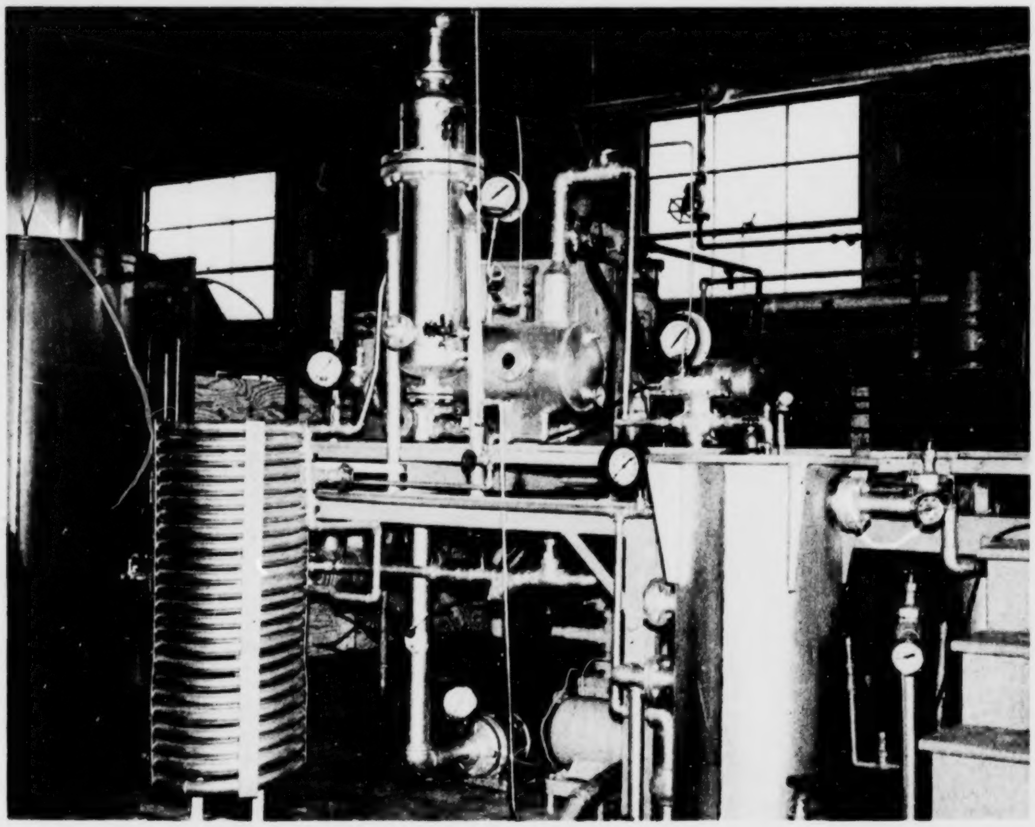


Figure 27. Single-stage flash still. The still shown here (horizontal chamber with sight glass) was used to make preliminary tests on distillation of primary effluent. The vertical unit in front of the still is the feed deaerator. By reducing the pressure on the feed water in the deaerator, oxygen and other gases that might cause excessive corrosion and reduced heat transfer in the still are removed.

ently considered promising; the present study is expected to provide a number of answers regarding technical feasibility.

Ammonia is a normal component of municipal waste water that presents a particular challenge in water renovation research, especially in the distillation process. Laboratory investigations involving simple batch distillation of secondary effluents have shown ammonia to be the principal contaminant in the first 10 percent fraction of distillate. Under laboratory conditions, acidification of the feed effectively eliminated ammonia from the product. Similar treatment is likely to be required during full-scale operation.

Freezing

THE FREEZING PRINCIPLE

When impure waters are frozen, the ice crystals formed have long been known to be composed of essentially pure water. This principle has frequently been used for laboratory scale purification of water and solvents of all kinds. In recent years, this process has been recognized as having potential use for large-scale operation as a method of separating commercial quantities of water from undesirable components contained in solution. Much research and development work has been done to determine the applicability of freezing as a method of separating contaminants from water on a practical scale. In the desalination of sea water the freezing technique has shown promise of being economically competitive with distillation, and large-scale plants now under construction by the Office of Saline Water will evaluate freezing as a practical method of recovering potable water from the sea.

Three steps are involved in applying freezing to the purification of water. First, heat is removed from the feed water to cool it to its freezing point. Additional heat is then removed by the vaporization of a refrigerant directly in contact with the feed, causing fine crystals of ice to freeze out of the solution. The refrigerant may be a low-boiling hydrocarbon such as butane or it may be water itself. When roughly half of the water has been frozen to ice, the ice-water slurry is transferred to another vessel (the washing column) where the unfrozen liquid is drained off and the crystals are washed by contacting them with pure water. As the final step, the washed ice is transferred to a third vessel where it is melted to form the purified product.

STUDY PROJECTS

To investigate the applicability of the freezing process to the renovation of municipal waste waters, the AWTR Program negotiated a contract in 1961 with Applied Science Laboratories of State College, Pennsylvania. The major concern was related to the organic contaminants contained in municipal waste streams and the effects they might have on the process. The possibility existed that these materials might be incorporated into, or adsorbed onto, the ice crystals and thereby greatly complicate the separation process.

Although the results of that contract have been previously reported (AWTR-4, PHS Publication No. 999-WP-4), the findings are summarized here. The study showed that up to 85 percent of the organic contaminants and 90 percent of the inorganic contaminants could be removed from waste water by the freezing process. Removal efficiency for ABS showed, however, an erratic pattern under the conditions tested. In view of these preliminary findings and of the fact that the contaminant load naturally occurring in waste water is smaller than that in sea water, the cost of renovating waste water by freezing might be somewhat less than presently indicated costs of recovering fresh water from the sea by this method.

Although good organic removal was achieved on some of the tests made during this first study, the results were not sufficiently consistent to provide conclusive evidence that the technique could be depended upon to remove organic contaminants effectively to the extent desired. The test procedure had involved direct contact between a highly volatile organic refrigerant and the waste water with subsequent removal of any carryover refrigerant from the product water by airblowing, but the sometimes excessive and inconsistent carryover of organics into the product water indicated an external organic contamination of the product water, presumably by a petroleum contaminant in the refrigerant or possibly even by the refrigerant itself.

To define better the extent of organic carryover from the feed into the product water, a second study that eliminated the possibility of refrigerant contamination of the product was undertaken. Instead of direct contact between the two liquids, the refrigerant was circulated through a metal housing surrounding the sample container. The contract for this phase of work was with The Carrier Research and Development Company of Syracuse, New York. Figure 28 shows the flowsheet for the 15-gpd freezing equipment used in the Carrier Company study.

In this freezer, ice, which formed on the surface of the heat exchange element, was scraped off by a helical screw and fed upward into the washing column. Interestingly, ice produced from the freezing of municipal waste water formed comparatively large agglomerates that did not wash as thoroughly as expected. Similar agglomeration does not occur when more concentrated salt solutions (such as sea water) are frozen in the same equipment. Figure 29 shows the agglomerated crystals in the wash column, and Figure 30 is a comparison of agglomerated ice crystals with the distinct, separate crystals in a slush that lend themselves to more efficient washing. The agglomeration phenomenon is attributed to the almost negligible freezing-point depression of waste water. The agglomeration was theorized to be the result of the melting and refreezing of the ice during compression while it was being scraped from the wall of the freezer. This action melted the surface of the ice crystals and, upon release of the pressure, the water refroze, producing agglomerates. With a more concentrated brine, this would not occur.

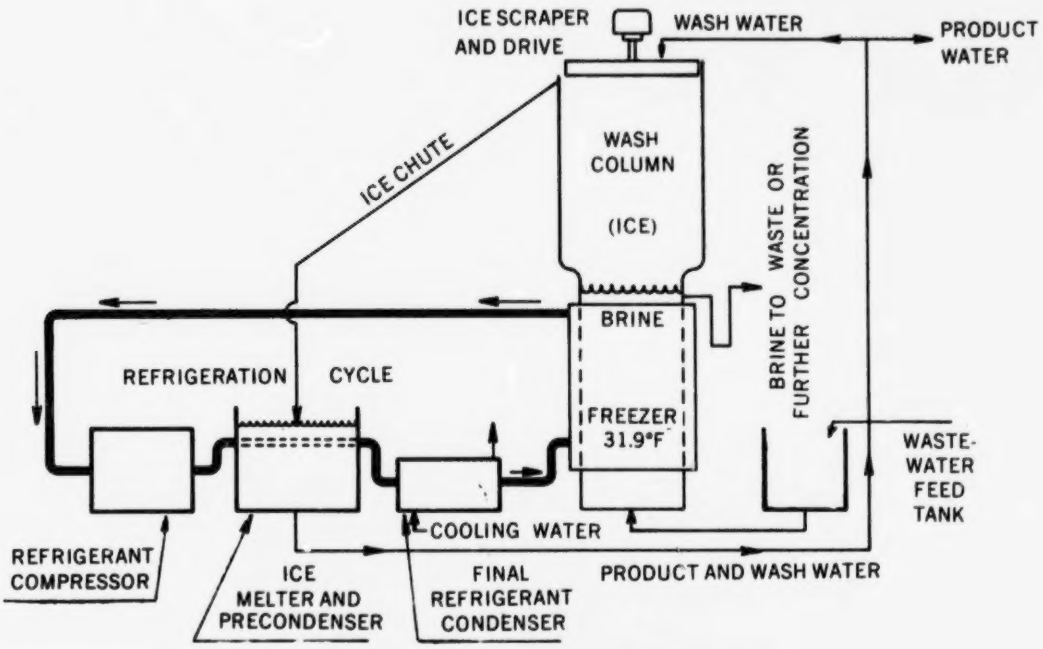

ICE SCRAPER AND DRIVE
WASH WATER
PRODUCT WATER
ICE CHUTE
WASH COLUMN
(ICE)
BRINE TO WASTE OR FURTHER CONCENTRATION
BRINE
REFRIGERATION CYCLE
FREEZER 31.9°F
WASTE-WATER FEED TANK
COOLING WATER
REFRIGERANT COMPRESSOR
ICE MELTER AND PRECONDENSER
FINAL REFRIGERANT CONDENSER
PRODUCT AND WASH WATER

Figure 28. Flowsheet of the continuous freezing process used by Carrier Research and Development Company to purify waste water by using noncontaminating freezing unit.

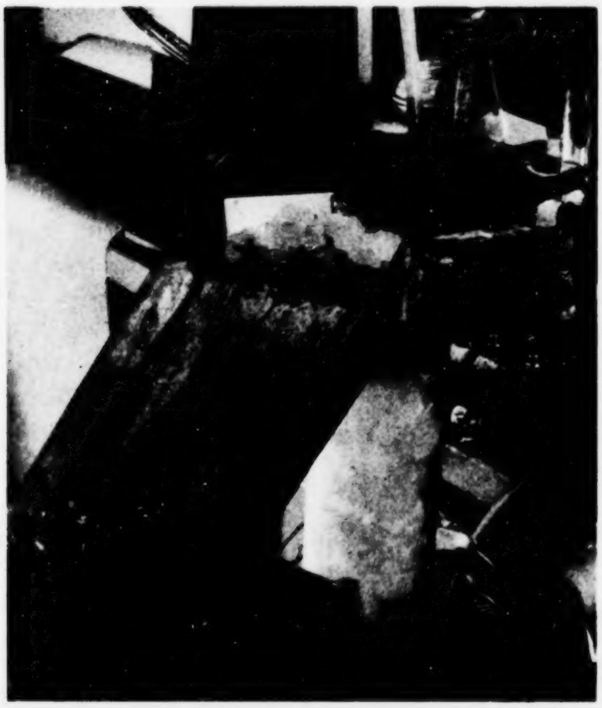


Figure 29. A closeup of the wash column during a run on the study of waste-water renovation by freezing. The agglomerated ice is easily seen. The scraper and the wash water return lines can also be seen. The freezer itself is directly below the wash column.

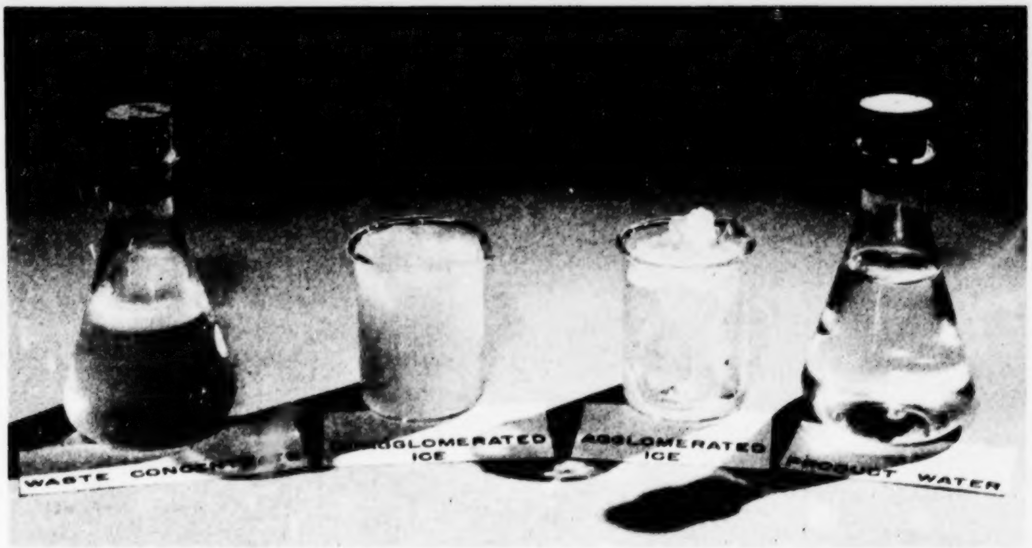


Figure 30. Freezing municipal waste water in Carrier Corp. freezer produces large agglomerated ice crystals making washing difficult; freezing of salt solutions of higher concentrations (such as sea water) produces individual unagglomerated ice crystals that are more readily washed. Also shown are samples of the product and residue streams from a freezing run with municipal waste water as feed. The higher detergent content of the concentrate is evidenced by the foam.

The tendency of the ice crystals to fuse in the test equipment proved to be a serious drawback to the washing out of impurities, owing to the entrapment of contaminant-bearing water in the interstices between fused crystals. Under these conditions the amount of contaminant carryover into the product water was relatively independent of the percent of melt returned as wash water as long as the wash rate was above a minimum value, which appeared to fall between 0 and 33 percent of the melt. This was particularly true for the organic contaminants. Data from several runs made with equipment having the configuration shown in Figure 28 are given in Table 3. These data illustrate the negligible effect of a wash rate above 33 percent of the melt.

Table 3. CONTAMINANT CONTENT OF WATER PRODUCED BY WASHING AGGLOMERATED ICE CRYSTALS WITH RECIRCULATED PRODUCT WATER IN VARIOUS RATIOS

	Wash rate — % of melt recirculated as wash water			
Contaminant, ppm	100	50	33	0
COD	22	34 to 40	35	63
ABS	1.7	2.2 to 2.5	1.9	3.6
Salts[a]	115	100 to 130	200	310
Total dissolved solids	--	60 to 160	200	400

[a] Measured by conductivity meter and expressed as NaCl.

To achieve more effective washing of the contaminants from the ice, a series of tests was made in which the agglomerated crystals were reduced to a smaller size by a mechanical chopper. This effort did not, however, produce optimum size ice crystals for most effective washing. These tests with chopped ice crystals showed the same general trend due to varying the recirculation of wash water, but the contaminant concentrations in the product water were generally less than those obtained with the unchopped crystals. Results for these latter tests are shown in Table 4.

Table 4. CONTAMINANT CONTENT OF WATER PRODUCED BY WASHING CHOPPED ICE CRYSTALS WITH RECIRCULATED PRODUCT WATER IN VARIOUS RATIOS

Contaminant, ppm	Wash rate — % of melt recirculated as wash water			
	100	50	33	0
COD	19 to 21.5	21 to 24	20	41.5
ABS	0.9 to 1.4	1.4 to 1.5	1.5	2.2
Salts [a]	31 to 47	53 to 60	53	270
Total dissolved solids	38 to 100	30 to 96	66	340

[a] Measured by conductivity meter and expressed as NaCl.

Eutectic Freezing

EUTECTIC FREEZING PRINCIPLE

An extension of conventional freezing termed "eutectic freezing" has, theoretically at least, the potential for simultaneously removing pure ice crystals and precipitated contaminants from concentrated waste streams. This is accomplished by operating at the eutectic temperature of the feed being processed. The principle is explained in Figure 31.

Eutectic freezing is not expected to serve as an initial separation process; rather, its possible use is as a method of concentrating waste brines before final disposal. Dr. Allen J. Barduhn of Syracuse University, under contract with the AWTR Program, proposed the eutectic freezing process for this application. His research on this subject has been directed to a confirmation of the following key assumptions:

1. At the eutectic point, ice crystals can be made to nucleate and grow independently of organic precipitates and salt crystals.

2. Waste waters containing no H_2SO_4, $MgCl_2$, or $CaCl_2$ will precipitate substantially all their inorganic salts at temperatures of about -10° F.

3. Substantially all dissolved organic matter will be "salted" out of solution at temperatures above the eutectic point.

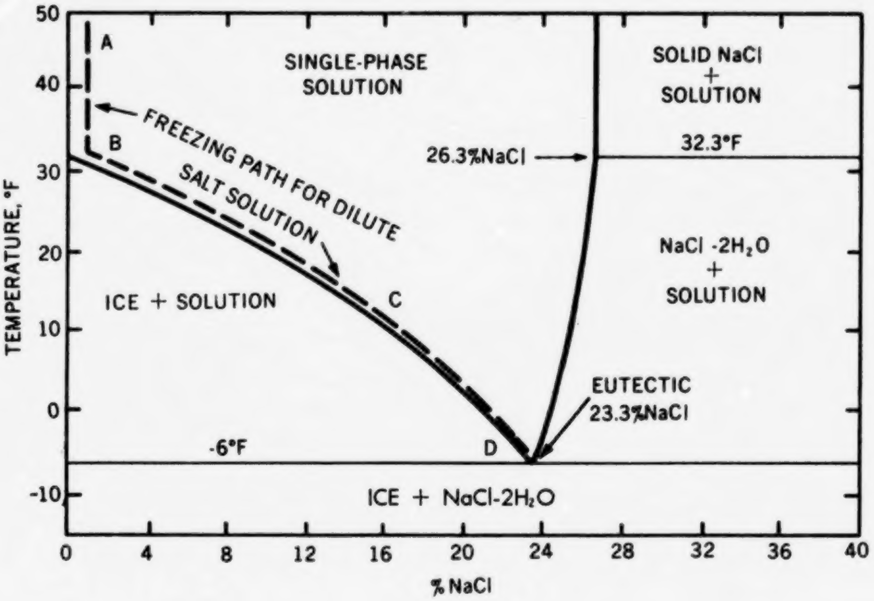


Figure 31. Eutectic freezing – phase diagram for the system $NaCl-H_2O$. To illustrate the principle involved, assume that a dilute solution of NaCl is to be treated to remove both water and solid salt by freezing. When the solution at point (A), for instance, is cooled to some temperature below 32° F (depending on the initial salt content), ice will begin to form. Along the line on Figure 31, this formation is seen to occur at point (B). As more ice is formed by further cooling, the composition of the remaining solution follows the curved path BCD until point (D) (the eutectic point) is reached. Up to this point, only ice has been formed, but further heat removal at the eutectic point (D) results in a stationary temperature at -6°F and the precipitation of both ice and $NaCl \cdot 2H_2O$ in a ratio that maintains the residual liquid at the fixed composition of 23.3 percent NaCl. The two solids formed can be separated by settling since the ice floats and the dihydrate sinks.

STUDY PROJECTS

Assumption No. 1 was investigated in detail by J. B. Pangborn[2] under an undergraduate research grant from the National Science Foundation. He found that simple eutectics of $NaCl-H_2O$, $KCl-H_2O$, and $NaHCO_3 - H_2O$ can be formed with mechanically distinct crystals of ice and salt and that the two solid phases separate quickly and easily, the ice floating and the salt sinking. In the case of simple salt solutions wherein the solid phase at the eutectic point is highly hydrated (e.g., $Na_2SO_4 \cdot 10\ H_2O$, $MgSO_4 \cdot 12\ H_2O$), the ice and salt phases do not separate well.

Dr. Barduhn investigated assumption No. 2 under a contract supported by the AWTR Program. Direct freezing was used to concentrate effluent from a trickling filter by a factor of 7, which produced a concentrate having a total dissolved inorganic solids (TDIS) content of 7,540

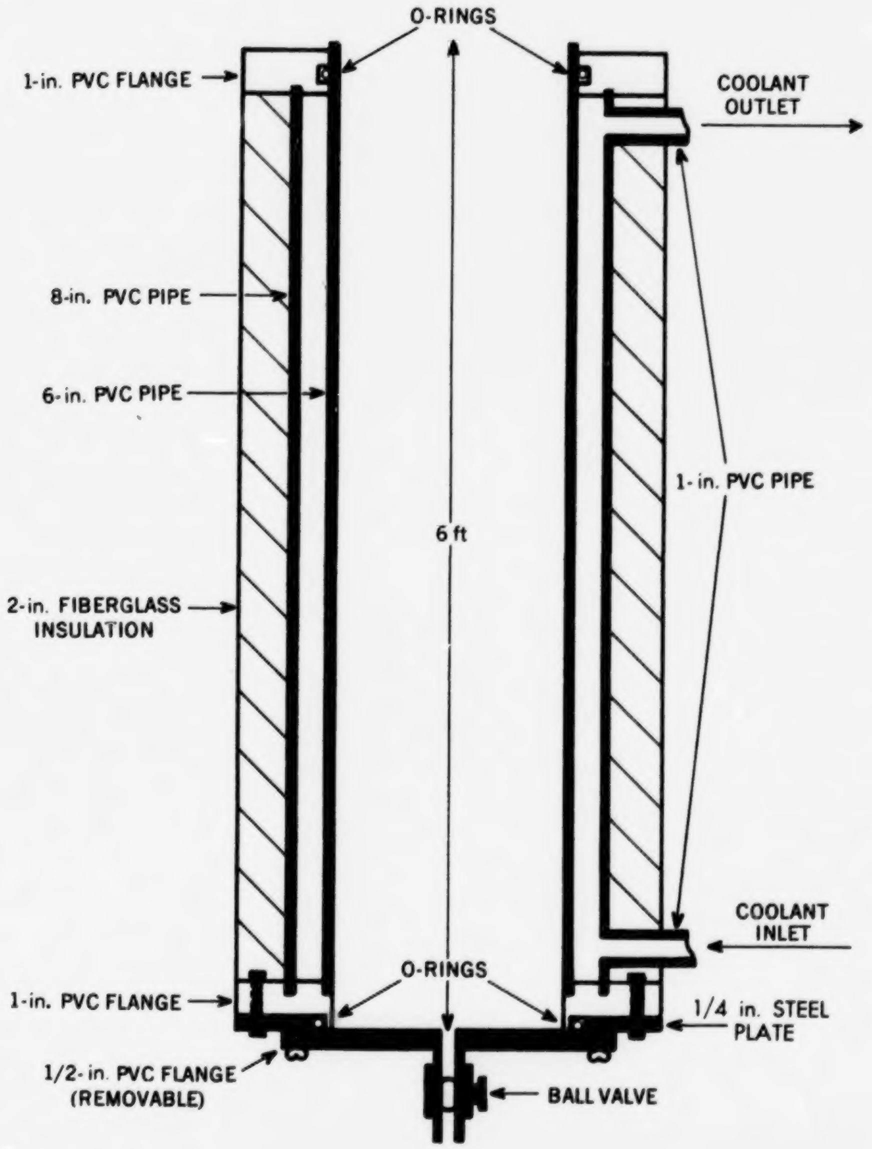

O-RINGS
1-in. PVC FLANGE
COOLANT OUTLET
8-in. PVC PIPE
6-in. PVC PIPE
1-in. PVC PIPE
6 ft
2-in. FIBERGLASS INSULATION
COOLANT INLET
O-RINGS
1-in. PVC FLANGE
1/4 in. STEEL PLATE
1/2-in. PVC FLANGE (REMOVABLE)
BALL VALVE

Figure 32. The 6-inch freezing column used in laboratory experiments to remove water from concentrated waste streams by eutectic freezing method.

milligrams per liter. To achieve eutectic conditions, this concentrate was placed in the 6-inch freezing column illustrated in Figure 32, and a 50 percent solution of ethylene glycol was circulated through the annular space between the columns until about 50 percent of the charged liquid had formed as ice on the walls. At this point, the unfrozen portion of the charge (mother liquor) was drained off to permit separate recovery of precipitated contaminants. The mother liquor was further concentrated by repeating this procedure through 10 separate stages.

The removal of water from this particular waste-water sample left concentrations of bicarbonate, sulfate, and magnesium ions well in excess of their equilibrium concentrations and thus prohibited the formation of a eutectic point at -6° F, the NaCl eutectic temperature. No individual analyses were made for organic materials, and the behavior of specific organics at relatively low temperatures was not determined. Apparently, however, there is little tendency for most of the gross organic matter to be forced out of solution. Approximately 90 percent of the organics originally present were left in solution after the last stage.

ABS formed a smaller and smaller percentage of the solids left in solution from stage to stage. This indicated that ABS is gradually forced out of solution by the combined effects of relatively low temperature and large inorganic ion concentration.

After stage 9, it was noted that magnesium was not being precipitated out. In an effort to promote precipitation, a stoichiometric amount of sodium carbonate was added to the concentrate from stage 9. Although this reduced the magnesium concentration from 20, 000 to 4, 380 milligrams per liter, the supersaturated $MgCO_3$ concentration was still too large to permit attainment of eutectic conditions in stage 10.

At a temperature of -9° F, the mother liquor in stage 10 was so viscous and gelatinous that processing it became almost impossible. This high viscosity was attributed to the comparatively large concentration of organic materials still in solution. The rate of crystallization was essentially nil, though the solubilities of some of the inorganic salts were certainly exceeded. At this point, over two-thirds of the original inorganic salts and over 90 percent of the ABS had precipitated, but only about 10 percent of the total organics had been salted out.

Even though an actual eutectic was not reached, freezing of the waste solution in stage 9 down to -6° F yielded a flowable concentrate containing 28 percent dissolved solids. Thus, the original volume of waste was reduced by a factor of about 30.

In a separate project to investigate assumption No. 3, Dr. Barduhn determined the effect of salt concentration and reduced temperature on the solubility of sodium dodecyl benzene solfonate (NaDBS) in water. Figures 33 and 34 give the results of this study. Obviously, both salt concentration and reduced temperature have a decided effect on NaDBS solubility. In view of the project previously discussed, however, NaDBS behaves differently from the other gross organics in waste water.

Ion Exchange

ION EXCHANGE PRINCIPLE

Many solid and some liquid materials, when placed in contact with mineralized water, are able to replace mineral ions in the water with ions originally in the material itself. This ion exchange process has been used for many years to soften hard water. In softening, the cal-

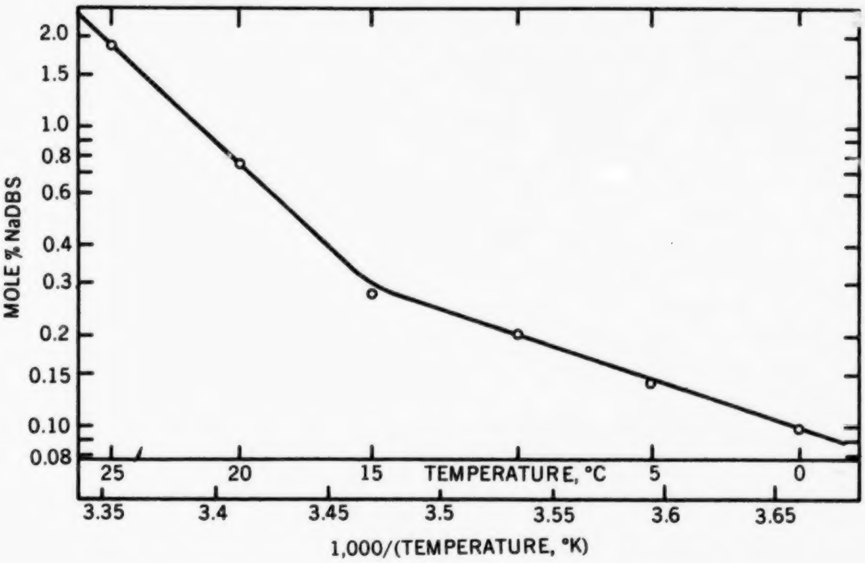


Figure 33. Solubility of NaDBS in pure water as a function of temperature.

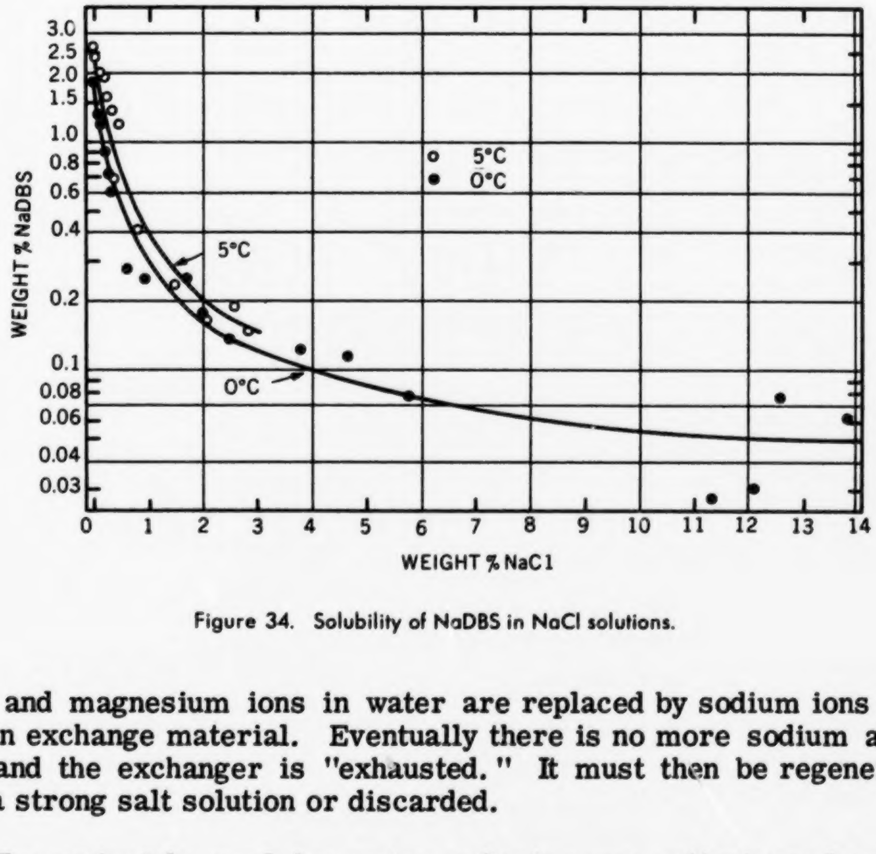


Figure 34. Solubility of NaDBS in NaCl solutions.

cium and magnesium ions in water are replaced by sodium ions from the ion exchange material. Eventually there is no more sodium available and the exchanger is "exhausted." It must then be regenerated with a strong salt solution or discarded.

The materials used for water softening are cationic exchangers. Several synthetic ion exchange resins have been developed that can remove either anions or cations from water. By combining a bed of hydrogen-containing cation exchange resins and a bed of hydroxyl-containing ion exchange resins, it is possible to deionize water almost completely. Since the hydrogen and hydroxyl ions entering the water from the resin combine to produce additional molecules of water, this technique completely removes the contaminating ions rather than exchanges one mineral ion in the water for another. When these resins are exhausted, they must also be regenerated, an acid being used to supply hydrogen ions to the cation resin, and a base, to supply hydroxyl ions to the anion resin.

This total deionization process could be used in the treatment of municipal waste waters for removal of ionic materials. Problems are, however, involved in the use of ion exchange that could make the cost prohibitive as an AWT process. The resins tend to become fouled by high-molecular-weight organic materials of the type commonly found in waste waters. Removal of as much as possible of the dissolved organics by pretreatment with activated carbon before contacting the waste water with the resins will, therefore, be necessary. Regeneration of the resins is an expense that cannot be avoided, and the cost of chemicals required for this purpose will represent a significant portion of the operating costs. Unless these regenerating chemicals, which themselves could create a secondary pollution, can be recovered and re-used, this cost could be prohibitively high. In view of these disadvantages, the ion exchange process has not been given high-priority attention.

STUDY PROJECTS

The limited research undertaken so far has involved investigations to determine the possible effectiveness of ion exchange as a method of removing high-molecular-weight organic ions from water. ABS was the organic material used. Results of a laboratory study by Ionics, Inc., demonstrated that the capacity of conventional ion exchange resins for removing ABS could be increased by as much as 50 percent by including in the resin formulation significant quantities of non-polymerizable materials such as isopropanol.

The principal findings from a study conducted at Polytechnic Institute of Brooklyn demonstrated that the affinity of anion resins for ABS is considerably less in some organic liquids such as ethanol and methyl ethyl ketone than in water. The significance of this is that a resin that has sorbed ABS can be regenerated more easily in the organic liquids than in water. Regeneration of resins in water, after ABS sorption, is very difficult. Because of the comparatively high cost of chemicals used for regenerating the exchange resins, possible methods of recovering these materials are of interest. A novel proposed method is being evaluated under terms of a contract with Chemical Separations Corporation. This scheme uses nitric acid as the cation resin regenerant and ammonium hydroxide as the anion resin regenerant, and proposes that the nitric acid be recovered by evaporating the nitrate-containing regenerant brine (after regeneration) and calcining the residue. Calcination would take place according to the following equation:

$$MNO_3 + H_2O \xrightarrow{heat} MOH + HNO_3 \qquad (1)$$

where "M" represents any of the metal ions removed from the waste water.

It is further proposed that the ammonium hydroxide be recovered from the anion resin regenerant brine by reaction with the alkaline product left after nitrate calcination. This reaction would proceed as follows:

$$NH_4\,A + MOH \longrightarrow MA + NH_4OH$$

where "A" represents any of the anions removed from the waste water.

Preliminary laboratory tests indicate that nitric acid recovery ranges from almost 100 percent to less than 50 percent depending upon the cation involved. Ammonium hydroxide recovery should be good. Still to be determined is whether the operating cost for the regenerant recovery method including acid makeup is low enough to decrease significantly the cost of regeneration.

Solvent Extraction

EXTRACTION PRINCIPLE

For some separation processes, the cost of operation decreases as the concentration of contaminants in the feed decreases. One such process is solvent extraction, a method whereby water can be separated from its contaminants by a solvent capable of "dissolving" the water but not the contaminants.

The solvent extraction process operates on the principle that certain organic solvents that contain strong electronegative atoms within the molecule are partially miscible with water to an extent depending mainly on the temperature and salt content of the water. One such solvent is di-isopropylamine (DIPA). A solubility diagram of DIPA and water at various salt concentrations is given in Figure 35. In practice, a water containing, for example, 1. 0 percent sodium chloride would be contacted with DIPA at 32°C (see Figure 35). At this temperature a separate phase containing 30 percent water and 70 percent solvent is formed. The water drawn into solution leaves the bulk of its contaminant load behind. The DIPA-water solution is then separated from the salt solution for recovery of the water. This recovery is accomplished by raising the temperature of the solution. At 55°C, the solubility of water in the solvent is decreased to 8 percent (see Figure 35), causing water to be released from the solvent. The water thus recovered contains a much lesser concentration of contaminants than it had originally. Solvent remaining with the product water is separated by air blowing.

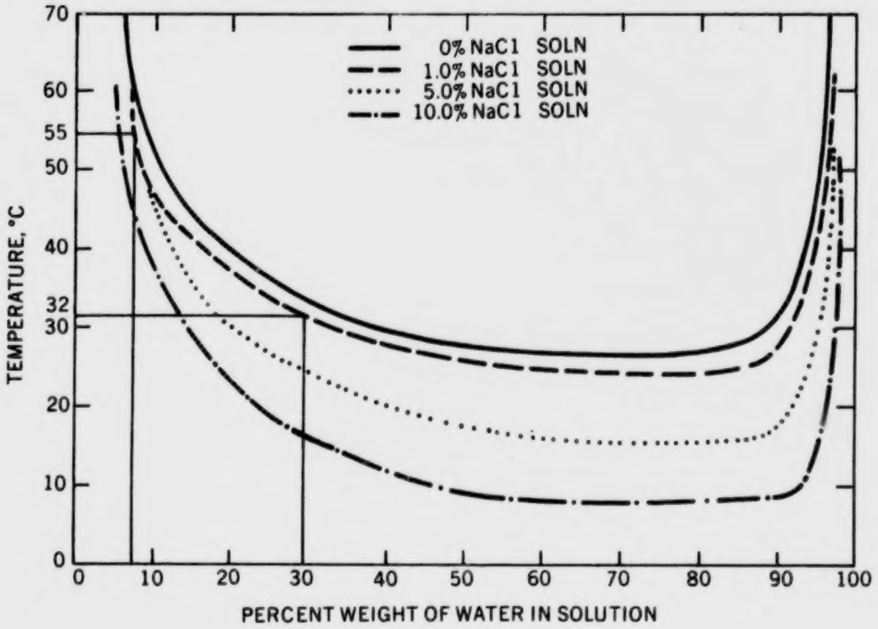


Figure 35. Solubility diagram of di-isopropylamine and water-NaCl system. Solvent extraction has potential use as a practical method of recovering pure water from municipal waste streams. These curves give the ratio of essentially pure water taken up by the solvent material at different concentrations of salt in the contaminated liquid.

A schematic diagram of the solvent extraction process is shown in Figure 36. In a continuous-flow, countercurrent system, the raw water and the solvent are intimately mixed in the extraction column under controlled temperature conditions. The extract discharged at the top of the column, representing the usable portion of the liquid stream, is then fed into a phase separation tank where the temperature is increased. At this point the water phase, now relatively pure, becomes the product stream and requires only air stripping to remove the residual solvent down to low ppm concentrations. Solvent recovered from the product stream, from the phase separation tank, and from the brine or raffinate (discharged at the bottom of the extraction column) stream, is recycled in the system. The brine, containing the concentrated contaminants, is wasted after recovery of the solvent.

STUDY PROJECTS

Extensive studies by Dr. Donald Hood and co-workers at Texas A & M University have demonstrated that solvent extraction has potential application in the desalination of brackish waters. Because of the dependency of treatment costs on contaminant concentration in the feed, however, solvent extraction has so far proven to be too costly to be considered a competitive process for desalination of sea water (total dissolved-solids content of sea water averages around 35,000 ppm compared with 800 to 1,000 ppm dissolved solids in municipal waste waters).

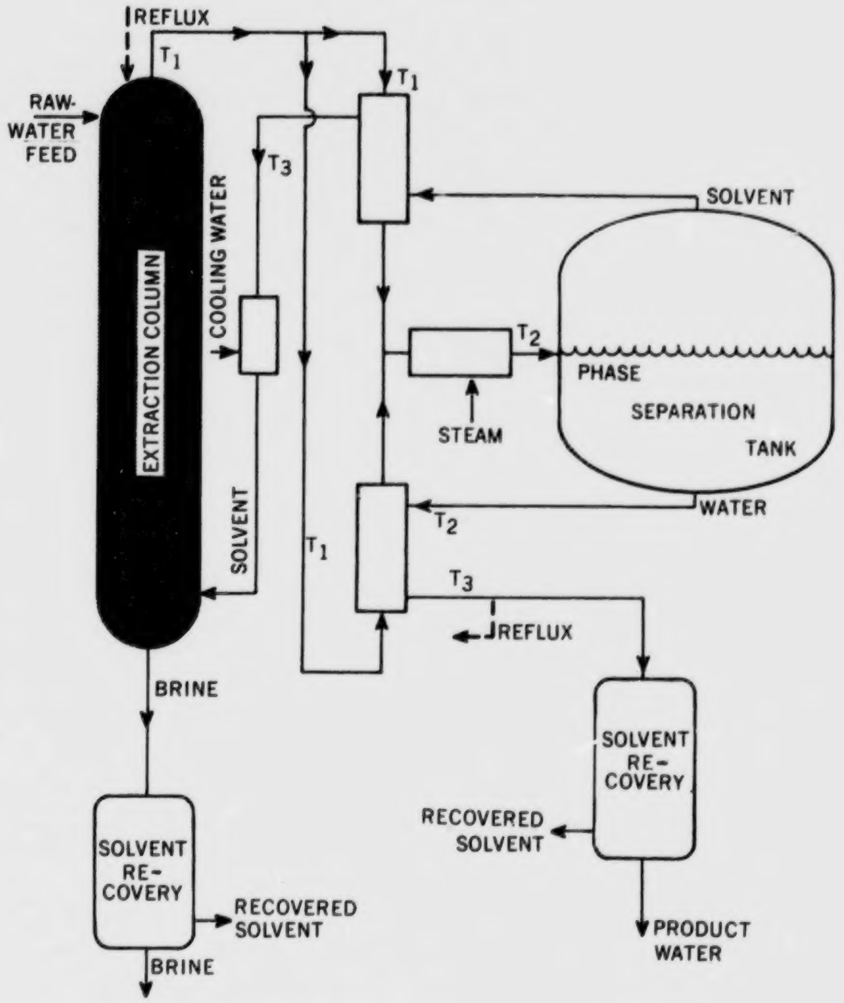

REFLUX
T1
RAW-WATER FEED
EXTRACTION COLUMN
COOLING WATER
T3
SOLVENT
T1
SOLVENT
STEAM
T2
PHASE SEPARATION TANK
WATER
T2
T1
T3
REFLUX
BRINE
SOLVENT RE-COVERY
RECOVERED SOLVENT
BRINE
SOLVENT RE-COVERY
RECOVERED SOLVENT
PRODUCT WATER

Figure 36. Schematic arrangement of continuous-flow solvent extraction process being studied as a possible method for advanced treatment of municipal waste water.

Investigations of solvent extraction as a possible method for advanced treatment of municipal wastes were initiated by the AWTR Program in July 1962 through a contract with Texas A & M University. Because of the many differences in the types and concentrations of contaminants between brackish water and waste waters, data obtained from solvent extraction studies on brackish waters could not be extrapolated or applied directly to waste waters. A program of basic laboratory research to establish the suitability of solvent extraction specifically for waste waters was, therefore, necessary. The presence of organic contaminants in waste waters raised questions about the effect they would have on the extraction solvents. Furthermore, equilibrium data on inorganic contaminants from brackish-water and sea-water studies had produced information mainly on sodium and chloride ions whereas a number of other ions in waste waters are of interest.

The initial laboratory studies with waste waters made by Dr. Hood involved batch extractions with trickling filter effluent from Bryan, Texas. With DIPA as the solvent, an extraction temperature of 35°C, and a separation temperature of 50°C, extraction tests were carried out under various water-to-solvent weight ratios ranging from 0.37 to 0.75. Organics in the feed, measured by COD, amounted to 85 ppm; the product COD was 10 to 20 ppm, and the raffinate or waste stream COD was 150 to 200 ppm. An ABS material balance on these runs showed that 5 to 10 percent of the feed ABS was carried over into the product, 5 to 10 percent stayed in the waste stream, and the remainder (80 to 90%) became associated with the solvent. Significantly, the process did not produce an organic-free product water, though the 10 to 20-ppm COD-measured organics was considerably less than the 85 ppm contained in the feed. This organic content of the product water represents carryover from the contaminants in the feed stream and does not include residual solvent. To make this determination, the samples were purged of the organic solvent before the COD analyses were made. On both product water and raffinate this was done by evaporating about one-third of the sample at a pH of 11 to 12. Although some of the more volatile of the organic contaminants were undoubtedly lost by this procedure, the quantity proved to be so small that it was not detectable by the COD test.

These batch extraction studies demonstrated that most of the ABS and a significant amount of the other organics (measured by COD) were retained in the solvent phase, a condition that indicated that periodic regeneration of the solvent would be necessary. In regard to the effect of solvent regeneration on the cost of the process under continuous-flow conditions, it has been established that some energy is available in the process that will allow regeneration by distillation, without the need for additional energy, if the solvent can be recycled as many as 10 times before regeneration.

Laboratory testing of the solvent extraction process under continuous, countercurrent flow operation was carried out in the equipment shown in Figure 37, by using the 6-foot-long Raschig ring-type extraction column for initial tests and the Rotating Disk-type Contactor on later work. Suspended solids were removed from the feed by Whatman paper filtration. The continuous-flow process achieved good removal of all waste contaminants except the nitrate ion. As an example, pollutant concentrations in the initial feed water, in the product water, and in the raffinate after approximately 14 cycles of the DIPA solvent are shown in Table 5.

During extended operation of the continuous-flow laboratory equipment, flooding of the extraction column occurred requiring the rate of throughput to be gradually reduced as the test progressed. The reason for this difficulty was due in part to the formation of a complex between the DIPA solvent and the phosphate ion causing a deposit of a waxy material on the Raschig rings. A further factor contributing to this difficulty was a gradual change in the physical characteristics of the solvent

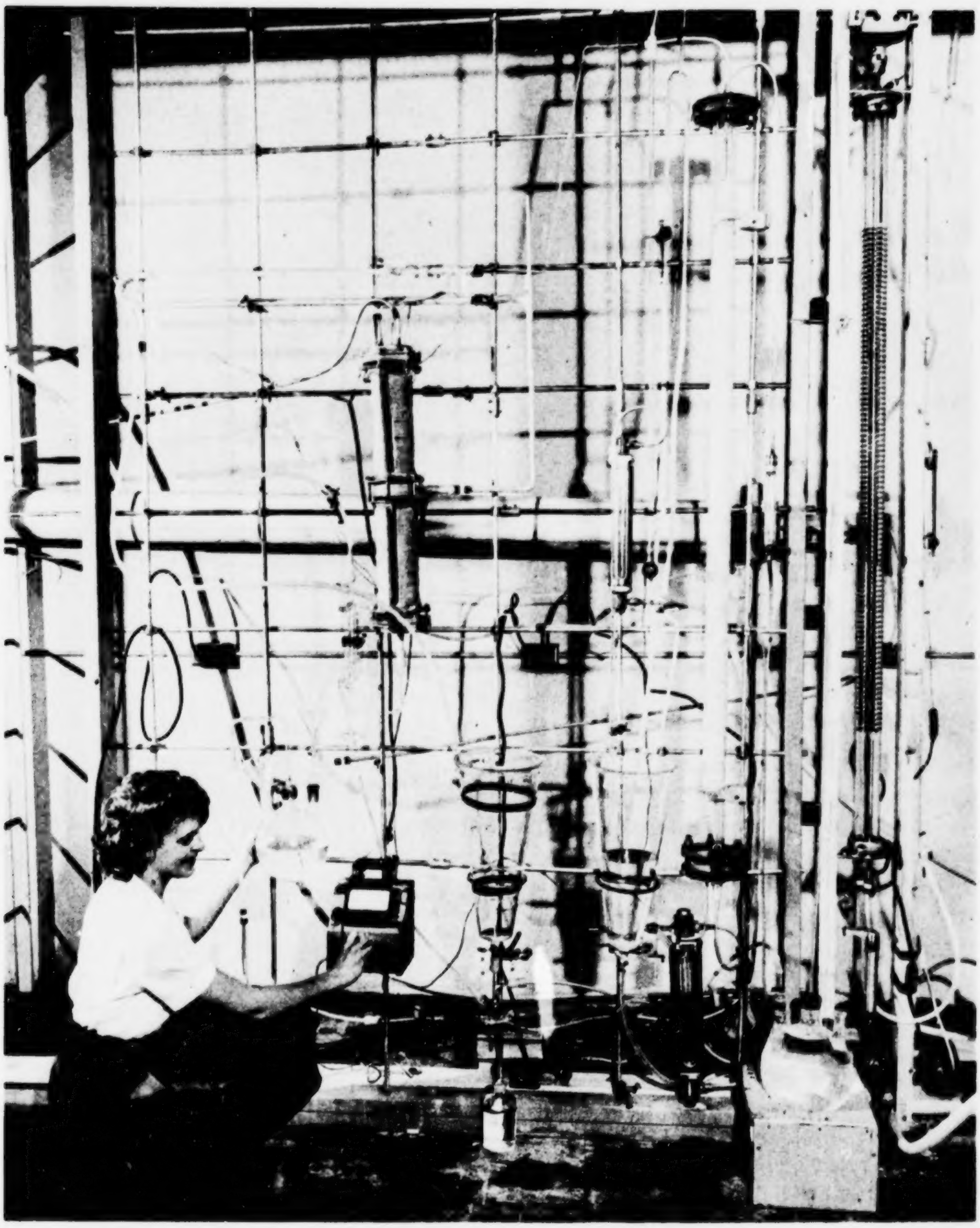


Figure 37. Laboratory equipment used for studying the solvent extraction method of recovering pure water from municipal waste water. The vertically mounted extraction column on the extreme right is termed a Rotating Disk-type Contactor. Just to the left of this RDC column is a second type of extraction column packed with Raschig rings. Both columns are made of glass tubing 2 inches in diameter by 6 feet long. The phase separation tank, center, is of glass tubing, 3 inches in diameter by 24 inches long. The large horizontal tube mounted behind the rack is the heat exchanger that cools the recovered solvent. Mrs. Vickie Egli, laboratory assistant, observes the instrument reading during a run.

(viscosity, density, etc.) that developed as the extraction progressed and was due to a buildup of organic contaminants in the solvent as they were removed from the water.

Table 5. CONTAMINANT CONCENTRATIONS IN MUNICIPAL WASTE WATER BEFORE AND AFTER TREATMENT BY SOLVENT EXTRACTION WITH DI-ISOPROPYLAMINE UNDER CONTINUOUS FLOW-OPERATION (AFTER 14 CYCLES OF SOLVENT)

Contaminant, ppm	Feed	Product water	Raffinate (waste)
COD	85	32	139
Cl^-	70	22	185
ABS	3.9	0.92	0.35
NO_3^-	43	39	47
PO_4^-	29	0.6	51
Total solids	595	92	1,770

Since the foregoing difficulties posed serious operational problems that could render the process almost inoperable after relatively short periods, consideration was given to methods of pretreating the feed water aimed at reducing the buildup of organic contaminants in the recycled solvent. To accomplish this, tests were made by using ferric sulfate coagulation followed by sedimentation before solvent extraction. This precoagulation and settling accomplished the desired objective of significantly reducing the concentration of organic contaminants, presumed to be colloidal, that stayed with the solvent phase. The reduction achieved was approximately 50 percent (see Table 6, which shows COD of the solvent for a series of tests made both with and without the ferric sulfate treatment). Note also that the 56-ppm COD-measured organics in the product water after solvent extraction was only slightly lower on these tests after extraction than the 61- and 72-ppm COD of the ferric sulfate-treated water before extraction. Later tests showed, however, that COD's of around 20 ppm were produced in the product water after the combination treatment involving precoagulation and solvent extraction.

Owing to the increased cost of the extraction process that would result if precoagulation were required, other, less costly methods of eliminating the problems encountered with the Raschig ring contactor are being studied. One possibility is the Rotating Disk Contactor shown in Figure 37. If successful operation is possible in this column without precoagulation of the feed, significant economies could be obtained. Work is currently under way with the Rotating Disk Contactor.

As pointed out above, extraction with DIPA has essentially no removal effect on the nitrate ion. Other amine solvents tested were similarly ineffective in removing nitrates. This problem has not yet

Table 6. DISTRIBUTION OF CONTAMINANTS BEFORE AND AFTER DI-ISOPROPYLAMINE SOLVENT EXTRACTION OF SECONDARY EFFLUENT, BOTH WITH AND WITHOUT FERRIC SULFATE PRETREATMENT

	Sample extracted with DIPA after								
	Filtration only			Filtration and pretreatment with					
				250 ppm $Fe_2(SO_4)_3$			375 ppm $Fe_2(SO_4)_3$		
Stage of treatment	COD,	ABS, ppm	Cl^-,	COD,	ABS, ppm	Cl^-,	COD,	ABS, ppm	Cl^-,
Untreated effluent[a]	123	4.9	58.5	123	4.9	58.5	114	4.9	58.5
Effluent after $Fe_2(SO_4)_3$ coagulation, but before solvent extraction	-	-	-	61.2	5.0	59.1	72	4.7	57.3
After solvent extraction:									
Product water	58.5	0.24	28	56	0.24	30.6	56	0.36	35.4
Raffinate	169	0.16	89.8	152	0.16	104.7	176	0.30	120
Solvent	63.6	3.1	0.0	30	2.35	0.0	34	2.56	0.0

[a] Contaminant concentration before treatment by either $Fe_2(SO_4)_3$ or di-isopropylamine.

been solved, but the possibility exists that other solvents, specifically those containing ether linkages, will prove more effective. Radioactive tracing techniques are being employed to investigate the selectivity of the amine solvents for other inorganic ions. Only the calcium ion has been investigated todate and it has proved to be more effectively removed than either sodium or chloride ions. Tests are scheduled on potassium, sulfate, carbonate, and other ions to determine their relative removal efficiencies.

At the present preliminary stage of development, solvent extraction appears to have the potential for successful application as a waste-water treatment technique. Based on the findings to date, the overall cost of waste-water treatment by this method is estimated to be less than 50 cents per 1,000 gallons of product water. This is, however, a preliminary projection, and better cost figures must await further development of the process to ascertain the extent of pretreatment and posttreatment that may be required. If potable water is to be produced, for example, posttreatment involving polishing by carbon adsorption will undoubtedly be required.

Oxidation

INTRODUCTION

Municipal waste waters contain many organic materials only partially degraded by conventional biochemical oxidation processes. Detergents such as ABS are a prime example. Chemical oxidation has the potential for removing these refractory organic materials from waste waters. The ideal chemical oxidant would oxidize all the organic molecules in waste waters to CO_2, H_2O, oxides of nitrogen, or oxides of other elements.

Oxidants such as ozone (O_3), chlorine (Cl_2), and potassium permanganate ($KMnO_4$) have been used for many years to improve taste and odor qualities or to disinfect municipal drinking water supplies. These oxidants improve water quality by destroying or altering the molecular structure of noxious organic chemicals. The concentrations of organics in drinking water supplies are, however, appreciably less than those in waste streams.

Chemical oxidants have not been generally used to improve the quality of municipal waste-water effluents because the cost of the necessary quantity of oxidant has been prohibitive. Recent and projected technological improvements in the production and application of active-oxygen-type oxidants, such as ozone, and the economic availability of large quantities of pure oxygen may, however, sufficiently reduce the cost of the chemical oxidation process to allow its application in advanced waste treatment.

Direct introduction of oxidants into waste streams may be applicable for destroying refractory organics either before or after treatment by other advanced treatment processes. Chemical oxidation may also be used for the destruction of concentrated organic wastes resulting from other advanced treatment processes. The destruction of industrial wastes, both organic and oxidizable inorganics such as sulfite or cyanide, is also possible with chemical oxidants.

Treatment of waste streams by direct application of chemical oxidants would have the advantage of removing organic contaminants without producing a residual waste concentrate. Furthermore, chemical oxidation effectively destroys any and all biological organisms in waste water.

Despite the many apparent advantages to be gained from the use of chemical oxidation, there are disadvantages, too. To begin with, waste water presents a difficult environment for successful chemical oxidation. The main difficulties result from: (1) The dilute concentration of organic materials, (2) the unknown composition and wide range of organic compounds present, and (3) the continually changing composition and concentration of organic materials in a given waste stream. The difficulty of identifying specific compounds either before or after chemical oxidation in such a complex situation has made necessary a reliance on gross parameters for evaluating the effectiveness of a given chemical oxidant. The following parameters are considered suitable:

1. Chemical oxygen demand (COD).[5]

2. Oxidant concentration.

3. Total organic carbon concentration (TOC).

The oxidation efficiency may be defined as:

$$\text{O. E. (oxidation efficiency)} = \frac{\Delta\text{COD, mg of } O_2/\text{liter}}{\text{available oxidation equivalents, mg of } O_2/\text{liter}} \times 100 \quad (2)$$

The ΔCOD is the change in the chemical oxygen demand of the waste effluent caused by the oxidation process. The available oxidation equivalents expressed in milligrams of O_2 per liter of effluent is the stoichiometric amount of chemical oxidation equivalents available from the charged chemical oxidant. In relation to the possible uses of renovated waste waters, the following requirements for a successful chemical oxidant are:

1. The oxidant should not produce any secondary pollutants that are difficult to remove.

2. The oxidant must be nonspecific in the oxidation attack on organic materials.

3. The oxidant should not appreciably contribute to the inorganic salt load in the waste water.

4. The contact and reaction time of the oxidant should not be excessive, preferably less than 3 hours.

5. The oxidant should be relatively easy to handle.

6. The oxidant should efficiently oxidize materials at the prevailing pH in the waste water (pH 7 to 9 for municipal wastes).

OXIDATION SYSTEMS

Six oxidation systems offer varying degrees of potential for the direct treatment of waste waters. Preliminary laboratory studies have been undertaken on some of these processes, and further work is either planned or under way. These systems are:

1. Oxidation by oxidants containing active oxygen (O_3, H_2O_2).

2. Accelerated molecular oxygen oxidation (autoxidation).

3. Catalytic oxidation of adsorbed organics by oxygen.

4. Oxidation by chlorine and its derivatives.

5. Oxidation by oxy acids and their salts, e.g., $KMnO_4$.

6. Electrochemical oxidation.

Three of these systems — the active-oxygen, the autoxidation, and the catalytic oxidation of adsorbed organics by oxygen—do not produce secondary pollutants and do not necessarily increase the inorganic salt load in the treated waste water. Since these oxidation techniques satisfy the other requirements for a successful oxidant better than the other potential oxidation systems do, they have been given priority in the conduct of laboratory research. Laboratory studies on oxidation systems have not, however, been limited to these three potential processes. As part of the preliminary technical and economic feasibility evaluations, some studies have been made on other possible systems. For example, the oxy acid oxidant, potassium ferrate (K_2FeO_4), was studied briefly in the intramural laboratory, and the electrochemical oxidation system was evaluated by contract with the Pennsalt Chemicals Corporation. A study is now in progress to evaluate the catalytic oxidation process for its suitability for oxidation of adsorbed refractory organics by O_2 at a temperature of 150°F.

Oxidation by Oxidants Containing Active Oxygen

Active-oxygen oxidation is currently the most promising of the suggested oxidation systems. Three practical sources of active oxygen are:

1. Hydrogen peroxide (H_2O_2).
2. Ozone (O_3).
3. Hydroxyl-free radical ($\cdot OH$).

Hydrogen peroxide. In aqueous media, H_2O_2 decomposes[3] to form the $\cdot OH$ radical. This radical is one of the strongest oxidants known in aqueous systems.[4]

Oxidation by hydrogen peroxide, with a catalyst of either ferric or ferrous salts, has been studied in the laboratory to determine the technical feasibility of using active-oxygen oxidation to remove the dilute refractory organics in (1) effluents from secondary treatment of municipal waste waters, and (2) effluents produced by various advanced methods of treating municipal waste waters. The equipment used in the study is shown in Figures 38 and 39.

Hydrogen peroxide alone does not oxidize the organic materials in waste waters within a practical reaction time. The system requires a multivalent metal salt (e.g., iron salt) catalyst. With iron salt catalyst a specific pH range of 3 to 4 is required to produce the $\cdot OH$ oxidant efficiently.

If ferrous salts ($FeSO_4$) are used, small measured portions of the salt solution can be added periodically to the H_2O_2-waste-water system. The ferrous ions rapidly react with the H_2O_2 to produce the necessary $\cdot OH$ radical. If a slower production (2 to 3 hours) of free radicals is

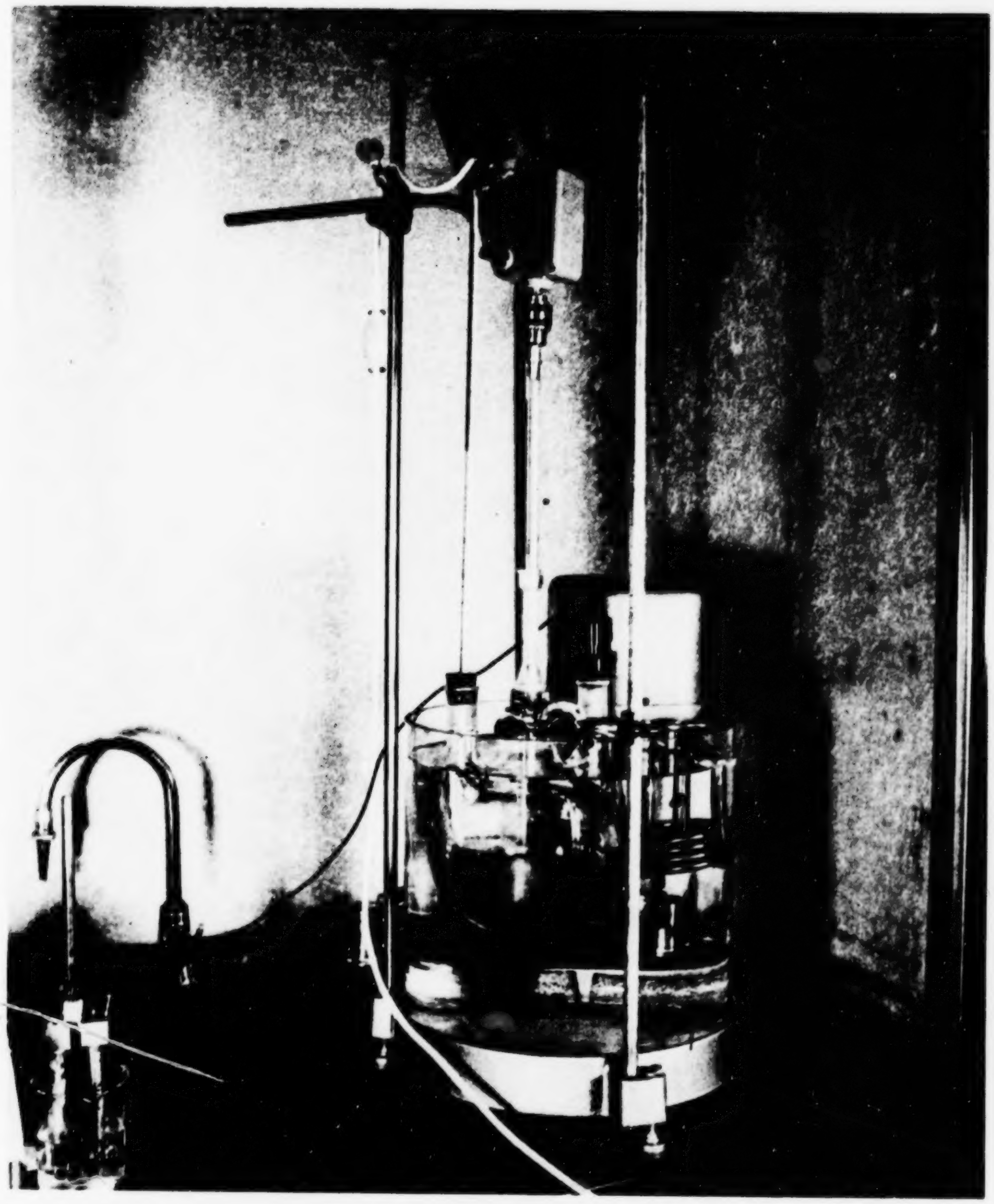


Figure 38. Apparatus for H_2O_2 oxidation and autoxidation studies. The system consists of a 2-liter, 3-neck, reaction flask, with ground-glass connections submerged in a constant-temperature bath, and a variable-speed stirrer. The waste-water sample can be oxidized in the reaction flask by the H_2O_2-iron salt system at temperatures from ambient to 100°C. The pH and temperature can be continuously observed. If an oxygen or inert (nitrogen) atmosphere is desired, the thermometer can be replaced by a fritted-glass gas sparger for continuous gas injection. The pH and temperature measurements can then be determined intermittently through the third neck of the flask. For kinetic studies, samples can be withdrawn periodically through the third neck for chemical analysis.

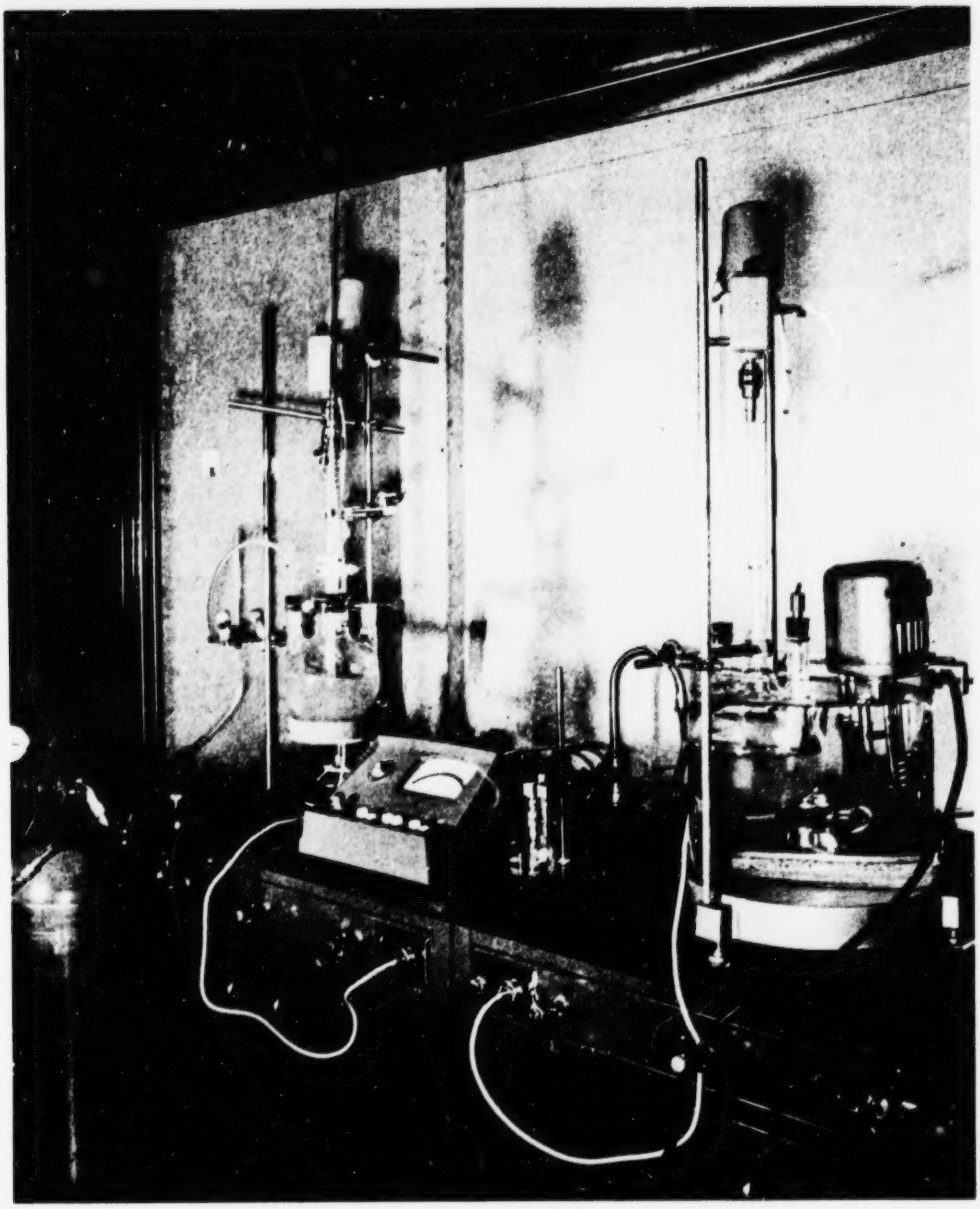


Figure 39. Apparatus for H_2O_2 oxidation and autoxidation studies. Complete laboratory systems for chemical oxidation of waste waters include a pH meter and gas cylinder. The reaction flask on the left with the large central neck contains a modification for allowing continuous addition of reagents through burets in the rubber stopper. The modification adds flexibility to the system. The H_2O_2-ferrous ion oxidation system requires periodic addition of small portions of ferrous ion and sodium hydroxide to the waste water-hydrogen peroxide mixture for efficient oxidation.

desired, ferric salts at a system temperature of approximately 65° C may be used to produce the radicals from the H_2O_2.

Results of laboratory tests with both ferric and ferrous salts and with stoichiometric H_2O_2 charges in the optimum (3 to 4) pH range are summarized as follows:

1. A 50 to 70 percent reduction in the COD-measured organic content of both filtered municipal secondary waste waters and of effluents further treated by carbon adsorption was achieved by the oxidation catalyst process.

2. Approximately 30 percent of the refractory organics present were converted to CO_2 and water.

3. The oxidation efficiency (use of available active oxygen) of the process varied between 50 and 70 percent.

4. A residual organic material remained after oxidation treatment.

5. ABS was preferentially attacked by the oxidant with 98 percent removal.

6. The residual organic (COD) of the secondary waste effluents after oxidation varied from 15 to 30 milligrams of O_2 per liter.

7. The residual organic (COD) of feeds previously subjected to carbon adsorption varied between 5 and 10 milligrams per liter after oxidation.

The use of H_2O_2 oxidation as an advanced method of treating secondary municipal effluents to remove refractory organic compounds appears to be technically feasible but is presently uneconomical. When H_2O_2 supplies 100 milligrams of available oxygen per liter, the cost of treatment is estimated between $1.20 and $1.50 per 1,000 gallons of treated waste water. Even though production of H_2O_2 on a scale required to treat from 100 million to 1 billion gpd of secondary effluent could reduce the treatment cost by as much as 50 percent, a cheaper source of active oxygen is still necessary for the process to be considered economically attractive.

Ozone. Although the exact oxidation mechanism of ozone is not thoroughly understood, ozone is known to be a highly effective oxidant[5] of refractory organics. Its decomposition in water may be a source of ·OH radicals, or the O_3 itself may be the actual oxidant. Based on present commercial (Welsbach) ozone production costs, the cost of supplying 100 milligrams of available oxygen per liter is estimated between 25 and 30 cents per 1,000 gallons of treated waste water in a 10-mgd facility. For a demand of 10 milligrams per liter, projected cost would be reduced proportionately to 2 to 3 cents per 1,000 gallons.

Corona discharge. Recent developments involving the use of high-frequency (10^4 cps), high-voltage (5×10^4 volts) corona discharge for the production of gasoline from powdered coal by free-radical attack have suggested the possibility of using corona discharge in water vapor as a possible source of hydroxyl radicals:[6]

$$\mathrm{HOH} \xrightarrow{\text{energy}} \mathrm{H}\cdot + \cdot\mathrm{OH}.$$

A preliminary estimate by the Advanced Technology Laboratories of the General Electric Company, developers of the high-frequency corona process, places the cost of supplying 100 milligrams of active oxygen per liter of waste water between 13 and 15 cents per 1, 000 gallons of treated effluent for a 10^7-gpd plant.

On the basis of presently estimated cost figures and preliminary technical results, application of the active-oxygen oxidation process appears to have some promise for removing the final organic residual from effluents produced by other advanced treatment processes. Effluents requiring only 10 to 20 milligrams of available oxygen per liter could be treated by the direct-corona process for 1. 5 to 3 cents per 1, 000 gallons.

Radiation from radioactive isotopes. Hydroxyl radicals may also be produced directly in aqueous solution during the adsorption of high-energy radiation from radioactive isotopes or from high-energy electron beams. Radiation (or high-speed electron beams or both) ionizes the water molecules and produces fast electrons in the process. The fast electrons, eventually slowed by collision with the aqueous media, are recaptured and produce hydroxyl and hydrogen radicals.[7] The net process is identical to hydroxyl radical generation by corona discharge:[6]

$$\mathrm{HOH} \xrightarrow{\text{radiation}} \mathrm{H}\cdot + \cdot\mathrm{OH}.$$

Fast electrons are produced chiefly by Compton scattering of gamma or X rays of 0. 5- to 10-Mev energy in water. The 0. 5- to 10-Mev gamma rays do not induce radioactivity in aqueous systems. Gamma rays of energy greater than 10 Mev also produce fast electrons both by Compton scattering and pair production, but at this energy level, radioactivity may be induced in the aqueous system. The inherent dangers of producing a radioactive water, and the need for increased shielding serve to discourage the use of gamma rays of energies above 10 Mev.

The fast electrons may also be produced directly as high-energy electron beams by Van de Graaff generators. Cobalt-60 ($\gamma = 1.33$ Mev) and cesium-137 ($\gamma = 0.661$ Mev) supply appropriate gamma radiation.

A study of radiation effects in sewage treatment[8] indicated that ABS removal and improved settling and filtration occurred during exposure to cobalt-60 gamma rays.

Preliminary evaluations, which have considered the cost requirements as well as shielding and handling problems, have led to the conclusion that use of a radioactive source such as cesium-137 for the removal of organics from waste waters is presently less promising than several other potential approaches. Successful irradiation treatment by gamma or electron beams would require accelerated long-chain autoxidation.

Accelerated Molecular Oxygen Oxidation (Autoxidation)

Autoxidation involves a free-radical-chain oxidation process[9] in which molecular oxygen acts as the chief oxidant. In the presence of excess O_2, the general autoxidation mechanism includes the use of hydroxyl radicals that initiate the reaction between O_2 and the organic compounds.

The autoxidation system was studied on secondary treatment plant effluents at nominal concentrations and also at relatively large concentrations. A hydrogen peroxide-iron salt system was used to supply the hydroxyl radical initiator ($\cdot OH$). Within the test conditions, pH was varied from 2 to 10, liquid temperature was maintained at 65°C, and oxygen was bubbled through the solution under two levels of pressure—atmospheric and 75 to 80 psig (see Figure 40). Organic removal was measured by the COD test after a 22-hour reaction period.

Results of these exploratory tests varied considerably. The principal findings were as follows:

1. The amount of oxygen combining with the organic material varied from less than that available from the H_2O_2 to 5 times more than available.

2. The test condition that resulted in the greatest use of oxygen involved the concentration of waste water by distillation to produce a preautoxidation COD of about 1,800 ppm.

3. For tests on secondary effluents conducted with approximately one-fifth of the total oxygen demand supplied by the charged H_2O_2, the H_2O_2 oxidation efficiencies approached 130 percent.

On the basis of these results, the autoxidation rates achieved with H_2O_2 were not adequate to qualify H_2O_2-initiated autoxidation as an economic contender for the removal of organic pollutants from waste waters. Hydrogen peroxide, with its restricted 3 to 4 pH range for efficient production of $\cdot OH$, is not best suited for initiating autoxidation. The suitability of other potential initiators will be investigated. Other factors needing further study include: the resistance to autoxidation of certain organic components in waste waters, the effect of chemical inhibitors, and the effects of pertinent variables such as O_2 pressure, temperature, and pH on the chain lengths and autoxidation rates in waste-water systems. Conclusions concerning the suitability of the autoxidation process for treating waste-water systems must be deferred until the subject has been more thoroughly investigated.

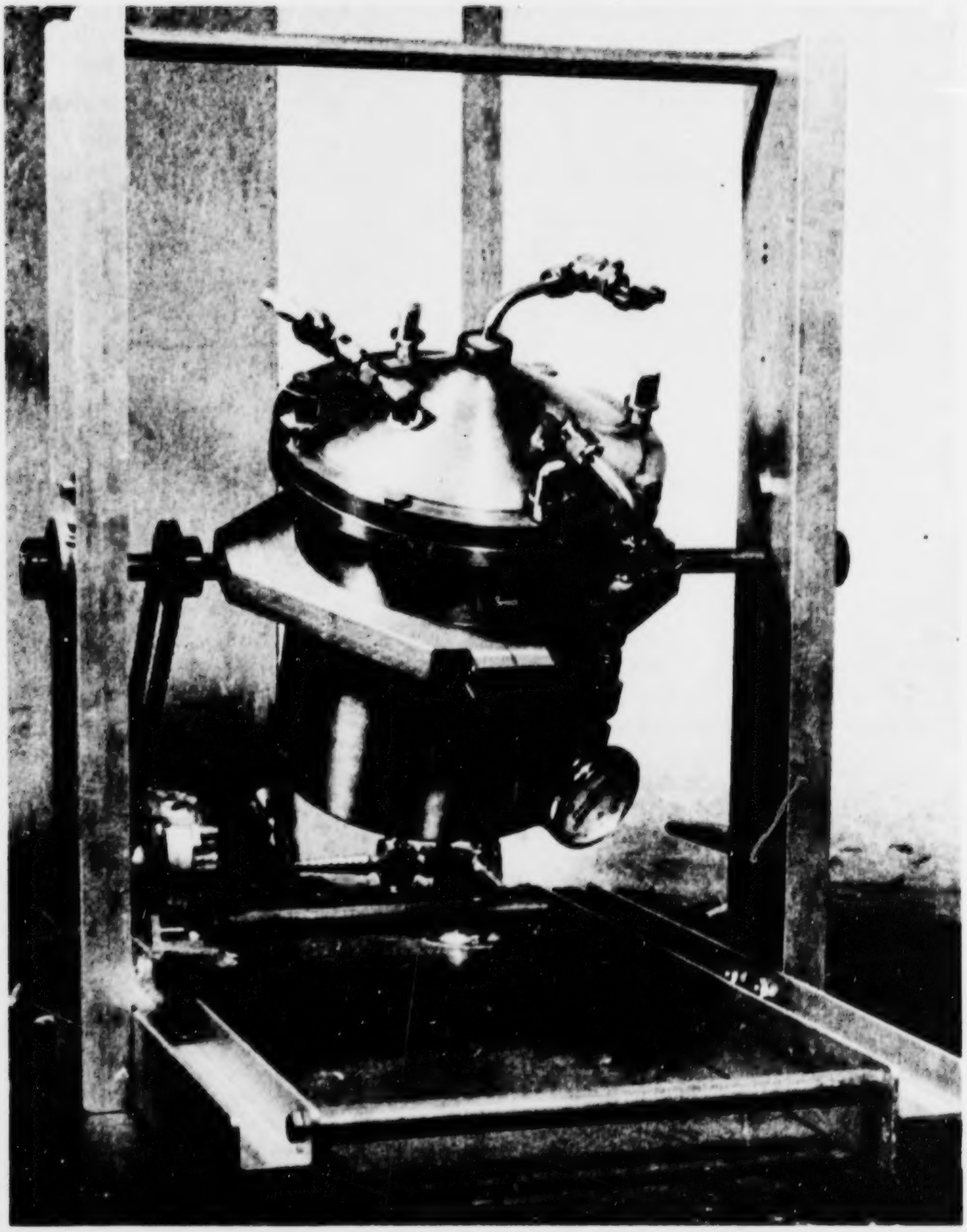


Figure 40. Chain-driven autoclave. The system was designed for use in the autoxidation studies to determine the effect of oxygen pressure and of temperature on molecular oxygen oxidation (autoxidation) of refractory organics in waste waters. The apparatus consists of a stainless steel pressure vessel with pressure gage and ports for adding oxygen and removing samples and a heat resistant motor with a chain drive mechanism. The system is placed in an oven set at the desired temperature. The waste-water sample and the autoxidation initiator are added. The system is sealed and pressurized with molecular oxygen. The pressure vessel is rotated to insure good gas-liquid contact. Periodic samples may be withdrawn from the sampling port.

If a suitable initiator and accelerating catalyst are developed, the cost of supplying liquid oxygen at 100 milligrams of O_2 per liter of waste water is estimated at less than 1 cent per 1,000 gallons of treated effluent for plant capacities of 10 mgd.

Catalytic Oxidation of Adsorbed Organics by Oxygen

Although oxidation of the refractory organics in waste waters by molecular oxygen is thermodynamically possible, the reaction rates are usually too slow to be of practical value. Reaction rates can, however, be accelerated in the presence of catalysts such as palladium or nickel, which reduce the activation energies required. Moreover, oxidation rates may be improved by concentrating the organics on the surface of solid adsorbents. Solid adsorbent impregnated with suitable catalysts may, therefore, be used to take advantage of both these phenomena.

Because of the many problems arising from the complexity and variability of waste-water systems and of the difficulties associated with the use of catalysts, the achievement of a completely continuous adsorption-oxidation process does not appear probable. In view, however, of the extensive studies under way on activated-carbon adsorption[10] and the comparatively low cost of molecular oxygen, a feasibility evaluation will be made on this potential technique.

Oxidation by Chlorine and Its Derivatives

Chlorine or its derivatives are added to most municipal water supplies in the United States to kill microorganisms probably by an oxidation attack of Cl_2 or HOCl on the living organic structure.[11] Important chlorine derivatives are the chloramines ($NHCl_2$ and NH_2Cl) and chlorine dioxide (ClO_2). Chlorine and its derivative are less powerful oxidants than the active-oxygen oxidants.

Chlorine and chlorine dioxide oxidize many of the organic chemicals contained in municipal waste waters but do not usually convert them to carbon dioxide and water.[12] The reaction of chlorine with organics may, however, produce organic molecules having considerable taste and odor, and other complex compounds may be formed.

The addition of stoichiometric amounts of chlorine will not oxidize all the refractory organics, and a large chlorine residual will be left.[13] Since oxidation by chlorine is less effective than that by active oxygen, and since the unknown oxidation products of chlorine may be highly toxic, chlorine and its derivatives are not presently considered as good prospects for removing the refractory organics in waste waters.

Oxidation by the Oxy Acids

The oxy-acid oxidants are usually added to aqueous systems as the salt of the oxy acid. Important oxy-acid salts with high oxidation potentials include potassium permanganate ($KMnO_4$) and sodium or potassium ferrate ($NaFeO_4$ or K_2FeO_4). The oxidation potentials of the oxy acids are strongly dependent upon the acidity of the aqueous system, increasing as the acidity increases (pH decreases). Thus the oxy acids have lower oxidation potentials at the neutral or alkaline pH ranges (7 to 9) occurring in municipal waste effluents than they do in acid solutions. A further disadvantage is that the oxy-acid salts increase the inorganic salt load in the aqueous system.

Potassium permanganate is used successfully as an oxidant in treatment of municipal water supplies to improve the color, taste, and odor properties and to remove dissolved ferrous salts, manganous salts, and H_2S.[13] In neutral or alkaline systems the oxidation product, manganese dioxide (MnO_2), acts as a coagulant and may be removed by settling or filtration.

Based on a preliminary economic evaluation, the potential for using $KMnO_4$ as an AWT oxidant is not particularly promising. References in the literature report only limited oxidation[14] of organics with $KMnO_4$, and a residual permanganate persists in the water even after 24 hours of reaction time. Since this residual $KMnO_4$ must be removed before the water can be re-used, the addition of suitable reducing agents is required and this step further increases the inorganic salt load in the aqueous system.

Although ferrate salts such as potassium ferrate (K_2FeO_4) are not commercially produced, their high oxidation potential and the coagulating properties of their oxidation products, highly insoluble $Fe(OH)_3$ (ferric hydroxide), make the ferrates potentially attractive as oxidants for treating waste waters.

Exploratory laboratory tests with K_2FeO_4 to treat filtered municipal secondary effluents with dosages supplying approximately 100 milligrams of available oxygen per liter showed the combination of ferrate oxidation and coagulation to be nearly as effective as the H_2O_2-iron salt system for removing organic materials from waste waters. Maximum organic removal as measured by the COD test was approximately 70 percent, occurring during a 5-minute reaction time at a pH of 2.2. Oxidation accounted for approximately 40 percent of the removal.

The comparatively high cost of oxy acid salts is a major factor limiting their application as an AWT process. The cost of $KMnO_4$ in carload lots to supply 100 milligrams of available O_2 per liter of waste water is estimated at 74 cents per 1,000 gallons of effluent treated. Although specific cost data are not available for the ferrate salts, order of magnitude estimates based on the cost of raw materials place costs for manufacture of these salts at $0.59 to $1.15 per 1,000 gallons of effluent. Owing to this unfavorable economic outlook, the oxy acids are, at present, essentially eliminated as oxidants for large-scale application in the treatment of municipal wastes.

Electrochemical Oxidation

Any material that increases the electrical conductivity of an aqueous solution may enter into a chemical reaction at the surface of electrodes placed in the solution. These chemical reactions are known as oxidation reduction reactions, and their study is called electrochemistry. Interest in electrochemistry as a possible technique for purifying municipal waste waters is based on the fact that many organic chemicals take part in electrode reactions, which often result in the complete degradation of complex organic molecules to carbon dioxide, water, and other oxides. The complete electrolytic oxidation of benzene and phenolic compounds has been reported in the literature. Phenol disulfonic acid has been electrolytically degraded to carbon dioxide, water, and sulfuric acid. The similarity between phenol disulfonic acid and ABS lends encouragement to the possibility that ABS could be similarly decomposed or oxidized, or both.

Electrochemistry has long been used for the commercial production of chlorine, caustic soda, hydrogen peroxide, and many other basic inorganic chemicals. Certain organic chemicals have been similarly produced on a commercial scale, but because of high production costs, electrolysis has been feasible only for organic products that could command a selling price of several dollars per pound. Recently reported[15] improvements in electrochemical technology may, however, result in substantial cost reductions. On the basis of these developments, several petroleum companies are perfecting electrolytic cells to make petrochemicals expected to sell for as low as 8 cents a pound. In addition to its commercial advantages, the lower cost technology anticipated for this process also improves its status as a potential waste treatment method.

The proposal to treat municipal waste water by electrochemistry is not new. This process was used in full-scale sewage treatment plants many years ago—the earliest record is a patent issued in 1889. Around 1911 at least one plant was operating at Crossness, a suburb of London, while similar plants in the United States were located at Santa Monica, California; Oklahoma City, Oklahoma; and Elmhurst, New York. At the Elmhurst plant, waste water was dosed with lime before entering the electrochemical cells, and the resulting product water was described as being "clear, odorless, and nonputrescent." All these early plants had been abandoned by 1930, however, on the claim that electrolysis accomplished no more than the lime pretreatment by itself, but confirmatory data to support this claim were not reported in the literature. Compared with the conventional treatment then employed, the electrolytic method doubled the cost of treatment.

In the mid-1930's investigators from the Soviet Union reported[16] on the use of an electrode process as a substitute for chlorine sterilization of bacteria in waste water. Satisfactory results were obtained in laboratory tests, and the process was to be scaled up, but no further report has been made on this project. The use of electrode processes for the treatment of a variety of industrial wastes has been reported, the principal ones being wastes from the alcohol fermentation and plating industries.[17,18] More recently, work has been done in Europe[19, 20] on the electrolysis of municipal waste water mixed with sea water. In this approach, precipitation of magnesium salts present in sea water aids in sludge flocculation. In addition, hypochlorite generated from the chloride ion oxidizes organics in the waste water and sterilizes the water. Two European plants now electrolyze waste water mixed with sea water, and one plant claims satisfactory separation of solids at a power cost of 6 cents per 1,000 gallons by using power costing 1 cent per killowatt-hour.

AWTR feasibility research on electrochemical oxidation of municipal waste waters was undertaken in May 1962 through a contract with the Pennsalt Chemicals Corporation. This study was of a tertiary treatment process rather than of a process intended to replace existing primary or secondary treatment processes, or both.

Tests were carried out in small laboratory-type electrolytic cells (Figure 41) with 3- by 3-inch electrodes. Filtered secondary effluent from a municipal sewage treatment plant was used for all tests. Initially, electrode packs having five anodes and six cathodes spaced about 1/4 inch apart were used, but subsequent tests involved cells containing only one anode and two cathodes (Figure 42). Liquid was continually recirculated in the larger systems but was kept agitated by stirring in the small beakers illustrated in Figure 41.

The Pennsalt study sought to establish the effects of electrode material, pH, current density, and temperature on the effectiveness of the electrochemical process in reducing COD, ABS, chlorides, and total dissolved-solids content of the secondary effluent involved.

Electrode materials. Since the material used for electrodes can be a major factor affecting both the technical and economic feasibility of an electrolytic process, the screening of prospective electrode materials was an important aspect of this study. The most likely mechanism for decomposing organic contaminants in such a system is by oxidation, and since the oxidation reaction occurs at the anode, greater emphasis was given to the study of suitable anode than of cathode materials.

Although it was recognized that the use of noneroding (inert) anodes would provide a definite economic advantage over eroding anodes, both inert and eroding materials were subjected to preliminary screening tests with the secondary effluent to observe any special advantages that might result from the use of eroding anodes. Eroding anodes of copper, lead, magnesium, steel, stainless steel, and aluminum were quickly eliminated from further consideration owing to their rapid disintegration during electrolysis. Tested at a current density of 6 milliamperes per square centimeter, each of these materials dissolved almost quantitatively with current.

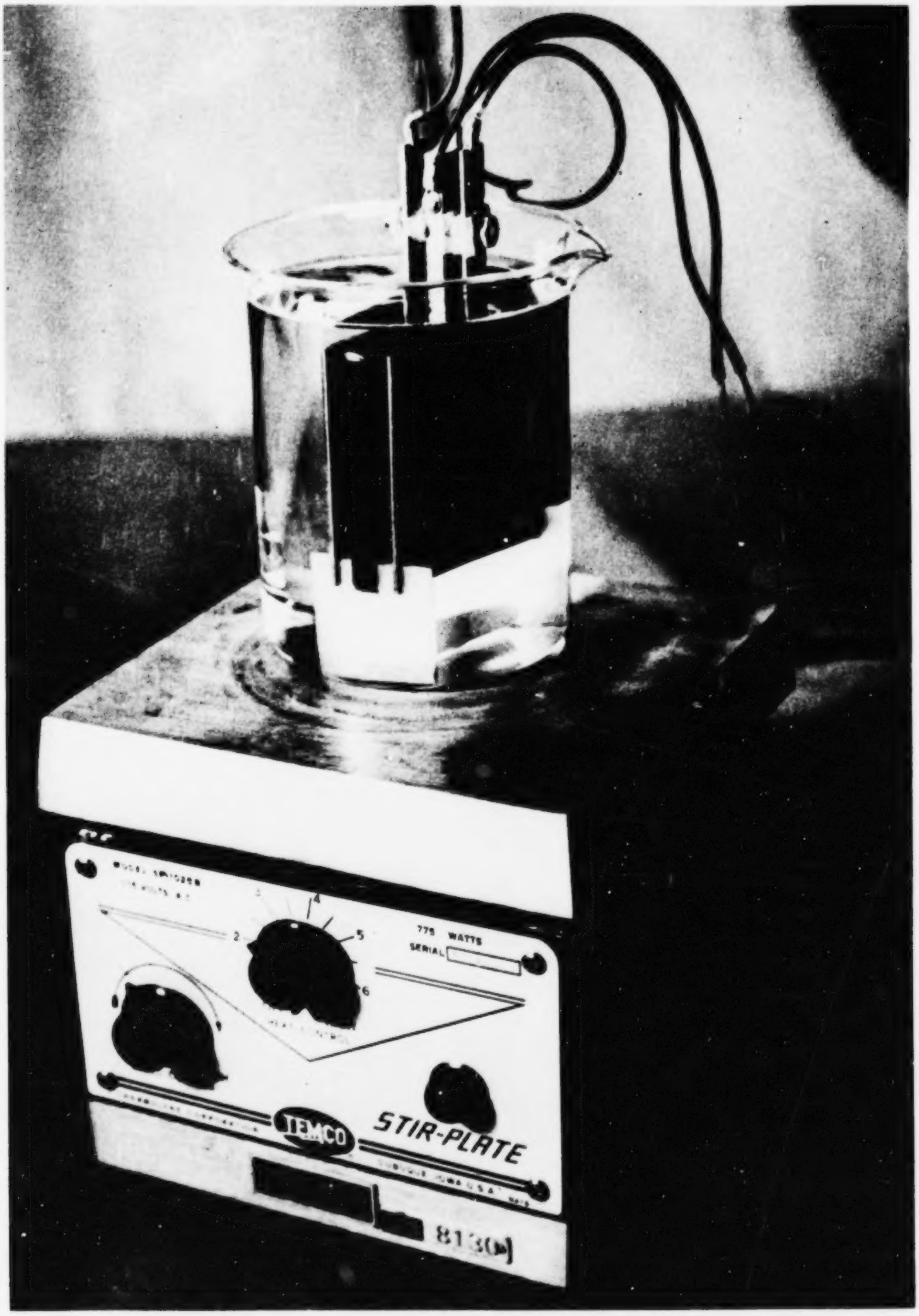

775 WATTS
SERIAL
2
3
4
5
6
HEAT CONTROL
TEMCO
STIR-PLATE
813(M)

Figure 41. Laboratory electrolytic cell with graphite anode and two platinum-coated titanium cathodes. Used for systems totaling less than 1 liter of waste water.

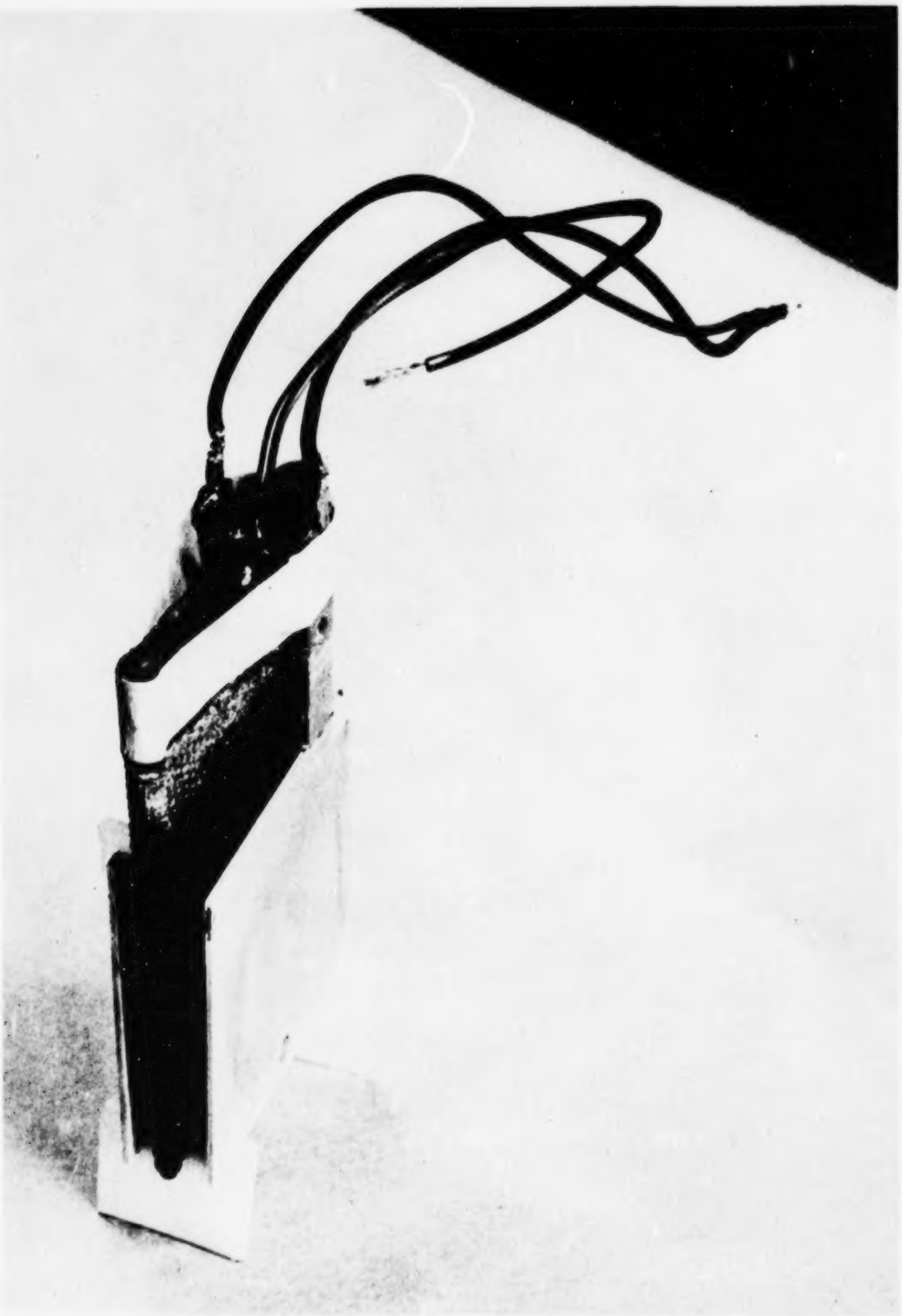


Figure 42. Electrolytic cell electrode assembly showing one lead dioxide anode and two steel cathodes.

Platinum, graphite, and lead dioxide were the inert materials evaluated, the platinum being plated onto titanium. Lead dioxide and platinum-coated titanium were the only materials tested that resisted disintegration sufficiently to be considered acceptable as anodes. Based on these test results and Pennsalt Chemicals Corporation's past extensive experience with a variety of industrial electrolytic processes, the contractor estimated that lead dioxide anodes could be expected to have a useful life of 1,000 days under ideal operating conditions. If the large-scale process encounters more severe conditions than occurred in the laboratory tests, a shorter anode life could result.

Graphite anodes commonly used in many industrial processes were found to be completely unsatisfactory for this application owing to severe flaking during electrolysis. Several types of graphite compounds were studied. In addition to the disintegration problem, many of the graphites used as anodes discolored the product water and some tended to increase rather than decrease its COD measurements.

During electrolysis the cathode is subject to less severe conditions than the anode is, and it was, therefore, unnecessary to make extensive studies to ascertain acceptable cathode materials. Maximum COD removal occurred when a platinum-coated titanium cathode was used in combination with a lead dioxide anode. An iron cathode used with the lead dioxide anode was, however, only slightly less effective in reducing COD. All electrode materials tested, except lead dioxide, worked satisfactorily as cathodes in secondary effluent, but not all were equally effective for contaminant removal.

The combination of a lead dioxide anode and a platinum-coated titanium cathode proved to be the best combination of materials studied in terms of resistance to disintegration and in effectiveness for removing contaminants. In this system, COD was reduced 80 percent, chlorides 90 percent, and ABS 90 percent. Total solids increased 6 to 8 percent, possibly owing to the incorporation of oxygen in the organic materials.

Effect of pH, current density, and temperature. The effects of pH, current density, and temperature on contaminant removal were evaluated in a series of laboratory tests with lead dioxide, graphite, and platinum-coated titanium anodes, all used in combination with platinum-coated cathodes. Each variable was tested at two levels for a given anode-cathode combination; these were as follows:

pH at 6 and 8 or at 5 and 8;

temperatures at 25° and 55°C;

current density at:

6 ma/cm^2 for 5 hours, and
30 ma/cm^2 for 1 hour, which provided
12,600 coulombs of electricity through
each 700-ml sample.

The results of these tests indicate that (1) current density, initial pH, and water temperature had little effect on contaminant removal in tests made with the lead dioxide anode, but the higher pH did effect a slight increase in dissolved solids in tests with the platinum-coated titanium anodes; (2) graphite electrodes were disintegrated under all test conditions but more severely at elevated temperatures and current densities; and (3) the anode material was the most important variable studied, lead dioxide and platinum or platinum-coated titanium being the only materials suitable for anodic applications involving municipal waste water.

Summary of electrochemical oxidation study. The principal results of this investigation are summarized as follows:

1. Electrochemical oxidation of filtered municipal secondary effluent reduced COD by as much as 80 percent, ABS by 90 percent, and Cl^- by 90 percent when lead dioxide anodes with platinum-coated titanium cathodes were used. All systems studied had little effect on total dissolved solids.

2. The cost of treating secondary effluent by the electrolytic method in a 10-mgd plant will vary between $0. 90 and $2. 40 per 1, 000 gallons depending on the completeness of treatment and the electrical conductivity of the waste water. To achieve approximately 50 percent COD removal would cost about $1. 20 per 1, 000 gallons compared with $2. 40 for 80 percent COD removal.

3. Lead dioxide was shown to be the most effective anode material for the reduction of ABS, COD, and chloride in waste water. It did not, however, reduce total dissolved solids.

4. Iron, lead, magnesium, aluminum, graphite, and copper all erode when made anodic in secondary effluent.

5. Lead dioxide, platinum, and platinum-coated titanium do not erode when made anodic for use with secondary effluent.

6. All electrode materials studied, except lead dioxide, worked satisfactorily as cathodes in secondary effluent; however, a platinum-coated titanium cathode in combination with a lead dioxide anode was more effective in reducing COD than an iron cathode with the lead dioxide anode was.

7. Oxygen and chlorine were produced at the anode and hydrogen at the cathode.

8. Plant costs based on the most optimistic assumptions will vary between $0. 90 and $2. 60 per daily gallon for a 10-mgd plant.

Conclusions regarding electrochemical oxidation. The major cost factors in electrochemical oxidation are for anode replacement and electrical power, which amount to 62 and 30 percent of the total cost respectively. Inasmuch as the estimated lead dioxide anode life of 1,000 days may be optimistic, the cost range of $0.90 to $2.40 per 1,000 gallons could be even higher if anodes disintegrated more rapidly.

In view of present knowledge, there appears to be little likelihood of reducing the cost of electrochemical oxidation unless some revolutionary development occurs. Development work under way by the Lead Industries Association on the use of lead and lead-silver alloys as electrodes for the treatment of waste waters will be followed for possible improved methods or new materials that may reduce existing cost figures.

At this time the cost of electrochemical oxidation for the purification of municipal waste waters appears to be excessively high in comparison with other promising methods of advanced waste treatment. In view of the foregoing findings, development work on this process by the AWTR Program has been discontinued.

CONCLUSIONS REGARDING POTENTIAL OXIDATION PROCESSES

The successful application of chemical oxidation as an AWT process will depend on both the economic and technical feasibility of a given oxidation process. The economic position of oxidation processes must necessarily be compared with other organic removal processes. Removal of organics by carbon adsorption is presently estimated[11] at about 10 cents per 1,000 gallons of treated secondary effluent at the 10-mgd scale. Estimated costs of waste-water treatment by each of the oxidant systems discussed are shown in Table 7. Two of the processes, Accelerated Autoxidation and Catalytic Oxidation of Adsorbed Organics, are economically promising. Determinations regarding their technical feasibility will, however, require considerably more extensive laboratory and field investigations.

Chlorine oxidation is considered to be not technically feasible for bulk organic removal from municipal waste-water effluents because of incomplete oxidation and excessive residual chlorine. Removal of organics by the oxy acids or by electrochemical oxidation is presently too expensive for this application.

From a technical standpoint, the active-oxygen oxidation system has considerable promise as an organic-removal process. With a greater oxidation potential than other practical oxidants, the active-oxygen system (·OH) is a more effective oxidant. If the corona process can be developed as a practical source of ·OH radicals for the treatment of waste waters, the active-oxygen oxidation system may be able to compete with present costs of activated-carbon adsorption for bulk organic removal in large-scale plants.

Further laboratory research on chemical oxidation of organics is being planned with studies scheduled on (1) accelerated autoxidation,

Table 7. POTENTIAL OXIDANT SYSTEMS

Oxidation system	Oxidant	Source	Estimated cost for 100 mg of available O_2 per liter, \$/1,000 gal.	Oxidation efficiencies, %[a] (approximate)
Active oxygen	·OH	Corona	0.13 to 0.15	70[7]
	O_3 or ·OH	O_3	0.25 to 0.30	70
	·OH	H_2O_2	1.20 to 1.50	
Autoxidation	O_2	liquid O_2	0.01	
Catalytic oxidation of adsorbed organics	O_2	liquid O_2	0.01	
Chlorine	Cl_2	Cl_2	0.12	
	$HClO(ClO^-)$	Cl_2		
Oxy acids	MnO_4^-	$KMnO_4$	0.74	
	$FeO_4^=$	Na_2FeO_4	0.59 to 1.15[b]	40
Electrochemical	$Cl_2(HClO)$ and ·HO (Probable)	Electrolysis of waste water	1.21 to 2.42	80

[a] Percent COD removal

[b] Raw-materials cost.

(2) catalytic oxidation of adsorbed organics, and (3) the active-oxygen process. Since the latter system (active oxygen) appears to offer the best potential for technical and economic success, it is currently receiving the greatest emphasis. A contract is scheduled with the Advanced Technology Laboratories of the General Electric Company to investigate the economic feasibility of the corona discharge process as a source of ·OH radicals for this application.

Future work will include studies to determine the oxidation mechanism by the active-oxygen system for the various classes of known refractory compounds found in waste waters. Moreover, the type of organic compounds that resist active-oxygen oxidation will be investigated and efforts will be made to identify the types or classes of organic compounds produced by active-oxygen oxidation.

MEASUREMENT OF ORGANIC MATERIALS IN WATER

The traditional measure of organic material in waste water has been Biochemical Oxygen Demand (BOD) expressed as milligrams of oxygen required for the biological oxidation of the contaminants. The 5-day BOD measurement determines, principally, organic compounds from biological sources including many compounds found in petroleum.

By its very nature, it does not determine organic compounds that are resistant to biological attack.

Various wet oxidation methods have been developed to measure the organic content of waste waters. The Chemical Oxygen Demand (COD) measures the quantity of dichromate reduced by the sample under carefully specified conditions. The test is run in strong sulfuric acid, and as a result, ammonia and many aromatic nitrogen compounds, including pyridine, are not oxidized. Nevertheless, the COD procedure gives a useful estimate of total organic content and is expressed in the same terms as BOD, namely milligrams of oxygen required to oxidize the 1 liter of sample.

The Standard Method[21] for COD requires a correction for chlorides that are oxidized by the reagent. The AWTR laboratory has developed a modification of the COD test that eliminates the need for a chloride correction by complexing chlorides with mercurous sulfate.[22] Because wet oxidation by dichromate in the Standard COD Method is incomplete, many attempts have been made to oxidize refractory materials by working at a higher temperature or in more concentrated acid. Unfortunately, these conditions lead to spontaneous decomposition of dichromate, and the quantity of dichromate reduced can no longer be equated with the quantity of organic matter oxidized. A research contract at Harvard University explored the use of high-temperature wet oxidation followed by determination of the carbon dioxide liberated. This method required an oxidation furnace to burn the volatile organic materials that distill from the wet system. Carbon dioxide is adsorbed and titrated after inorganic acids have been removed from the gas stream. The final result was a combined wet and dry oxidation chain that provides a measure of total organic content as percent carbon. The procedure uses conventional glass apparatus and is capable of one determination every 3 hours. Great care must be taken to eliminate leaks. Under ideal conditions carbon can be detected at a few parts per million.

The Dow Chemical Company has developed a dry oxidation system for organic carbon compounds in water that employs a hot-tube combustion furnace and an infrared nondispersive CO_2 analyzer.[23] A 20- to 40-microliter sample of water is squirted onto the hot packing of the combustion tube in a stream of pure oxygen. The sample is rapidly converted to steam, and the organic content is burned to CO_2. The O_2 stream, containing a pulse of CO_2, then passes to the infrared cell where it is measured as peak height on a strip chart recorder. The instrument is sensitive to 1 milligram of carbon per liter and has a precision of ±5 percent. Carbonates in the sample are removed by acidification followed by aeration with pure oxygen. All organic materials tested are quantitatively oxidized. The small size of the sample makes the method unsuitable, however, for many waste waters containing suspended solids because of problems encountered in obtaining a homogeneous sample.

ULTIMATE DISPOSAL

The philosophy that calls for the development of advanced methods of treating municipal waste waters incorporates several broad concepts regarding the need for these treatment methods; these include (1) the need for more effective waste treatment to effect better water pollution control and (2) the desirability of providing practical methods for accomplishing water re-use. For an AWT system to meet the requirement of achieving the "water pollution control" concept, special consideration must be given to the disposal of the concentrated wastes that will be produced.

In striving for the maximum degree of water pollution control, the AWTR Program has established a goal of permanent waste disposal designed to guarantee against any future contamination of water supplies, either surface or ground waters. This final disposition of waste concentrates has been termed "ultimate disposal" and is defined as "the treatment, handling, or placement of a waste in such a manner that it never thereafter comes into contact with human activities while in its noxious form, other than, in certain instances, for a very small surveillance or containment activity." With such severe limitations, the possible solutions are essentially limited to the following:

1. Subsurface storage in cavities or pervious strata sealed against leakage.

2. Conversion of the wastes to innocuous compounds by oxidation or other chemical reactions.

3. Surface storage in isolated locations in ponds sealed against leakage and leaching.

4. Disposal of the unconfined wastes into the ocean where they would be diluted to negligible concentrations.

5. Conversion to useful products by mixing or combining with other materials for use as construction materials, chemical raw material, or other usable products.

Studies have been carried out to evaluate a number of potential disposal processes to establish their technical and economic feasibility for this specialized usage. These have, in all cases, been desktop studies designed to assess the physical, natural, and economic parameters that might bear on the costs, physical magnitudes, and general feasibility of ultimate disposal of advanced treatment wastes. Preliminary cost estimates have been determined for reasonable ranges of the parameters, the costs, and physical magnitudes involved, especially as these are influenced by volume and concentration of waste. These evaluations provide the first step of a program to develop eventually practical methods of disposal; they will be followed by laboratory and pilot plant investigations, finally leading to the construction and operation of large-scale disposal processes.

WET OXIDATION

Wet oxidation is a process whereby concentrated organic contaminants can be converted to innocuous compounds. Details of the considerations involved in a feasibility evaluation of the wet oxidation process have been previously reported, but are summarized here for the sake of completeness and to provide a comparison with other potential waste disposal processes.

Commonly known as the Zimmerman process, this technique makes possible the oxidation of organic matter occurring in aqueous dispersion without the necessity of separating the organic matter from the water. It can thus serve to dispose the organics in concentrates produced from municipal wastes. The process operates in a closed high-pressure system and, since oxidation takes place in the water itself, there is a minimum of air pollution or odor problems. Concentrated sludge and compressed air are fed continuously into a reactor as shown in Figure 43. The mixture is preheated in heat exchangers to about 400° F to help start oxidation; oxygen combines with organic material in the sludge to form inorganic ash plus carbon dioxide, nitrogen, and steam. Once started, the process does not usually require outside heat to keep it going if the feed sludge exceeds a certain minimum organic content. At operating pressures of 1,200 to 1,800 psig and temperatures from 500° to 700° F, approximately 80 percent oxidation of organics requires 7 to 10 minutes' reaction time. Smaller systems operating at 500 to 600 psig and 420° to 450° F require 2-1/2 hours' detention time to achieve roughly 60 percent oxidation of organics.

In making an analysis of costs for a wet oxidation process to treat concentrated AWT wastes, calculations were made for nine hypothetical cases involving concentrated waste flows of 1,000, 100,000, and 10 million gpd, with the assumption of organic concentrations of 100, 3,000, and 100,000 ppm, and corresponding inorganic loadings of 200, 6,000, and 200,000 ppm. Experience in the use of this process for disposing this kind of wastes has been limited. Consequently, reactor design data based on 80 percent removal of COD, process cost data, and other process parameters were developed from pilot plant data reported in the literature, from design data for plants not yet in operation, and from laboratory data and other information furnished by the developers of the wet oxidation process.

The process design showed that for a fixed ratio of inorganics to organics in the feed, here 2.0, there is an upper limit of organic concentration that can be wet oxidized without oversaturation with respect to the inorganics. This limiting concentration is 60,000 ppm organics (6%) for the conditions chosen for this study. A minimum concentration of organics (about 4 percent) also exists, as mentioned above, to keep the reactor self-sustaining.

Figures 44 and 45 show the relationship of estimated unit plant costs and unit processing costs to plant capacity, over the range of

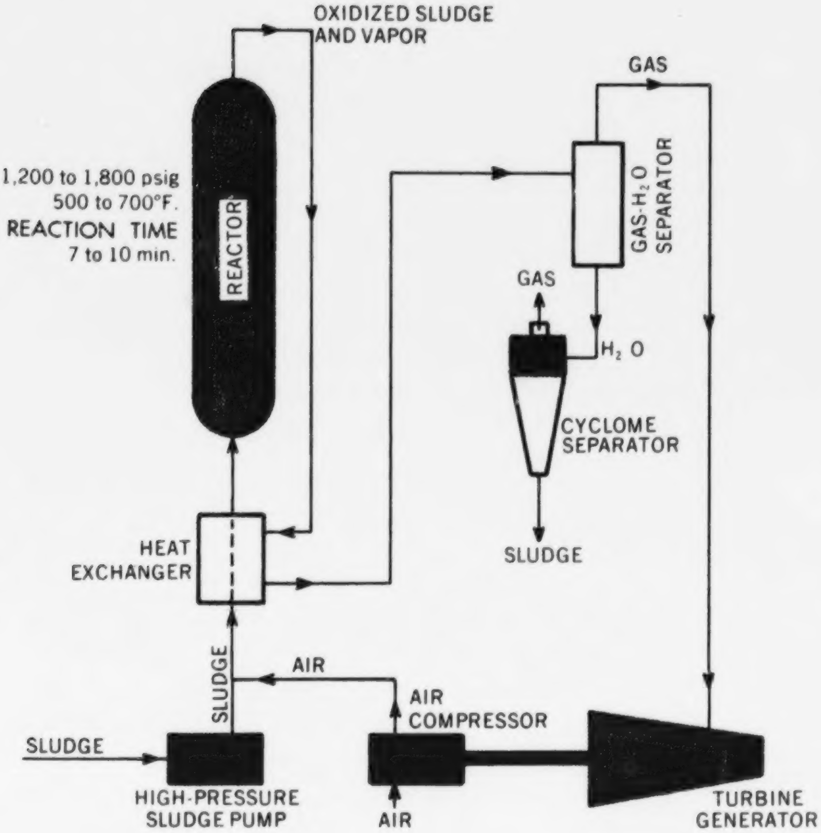

OXIDIZED SLUDGE AND VAPOR
GAS
1,200 to 1,800 psig
500 to 700°F.
REACTION TIME
7 to 10 min.
REACTOR
GAS-H₂O SEPARATOR
GAS
H₂O
CYCLOME SEPARATOR
SLUDGE
HEAT EXCHANGER
SLUDGE
AIR
AIR COMPRESSOR
SLUDGE
HIGH-PRESSURE SLUDGE PUMP
AIR
TURBINE GENERATOR

Figure 43. Schematic arrangement of Zimmerman wet oxidation process. This process is under consideration as a possible method for the ultimate disposal of concentrated wastes produced by the advanced treatment of municipal waste waters. In this process, organic materials are oxidized to innocuous compounds.

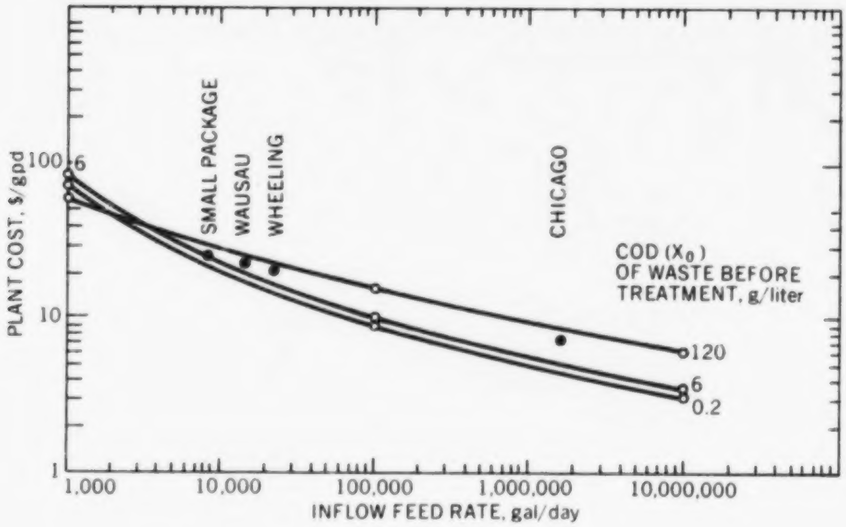


Figure 44. Ultimate disposal by wet oxidation: relationship of cost to size of wet oxidation plants.

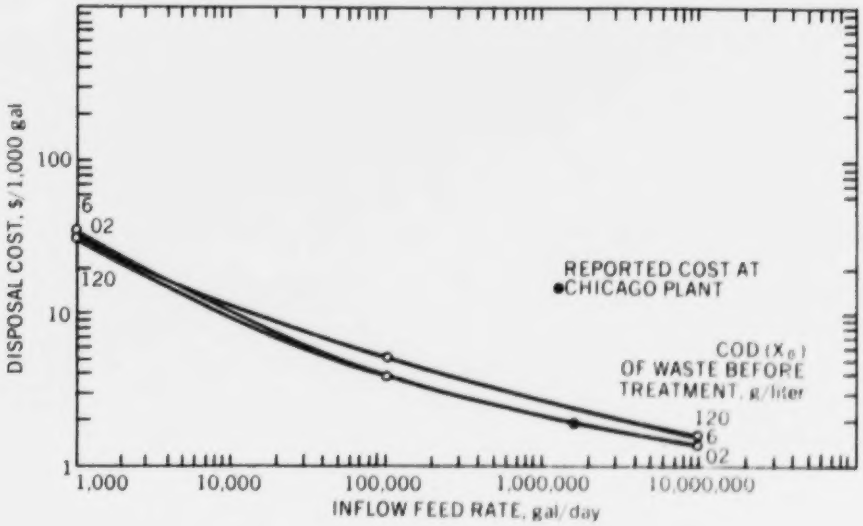


Figure 45. Ultimate disposal by wet oxidation: disposal costs per volume of processed waste as related to size of wet oxidation plant.

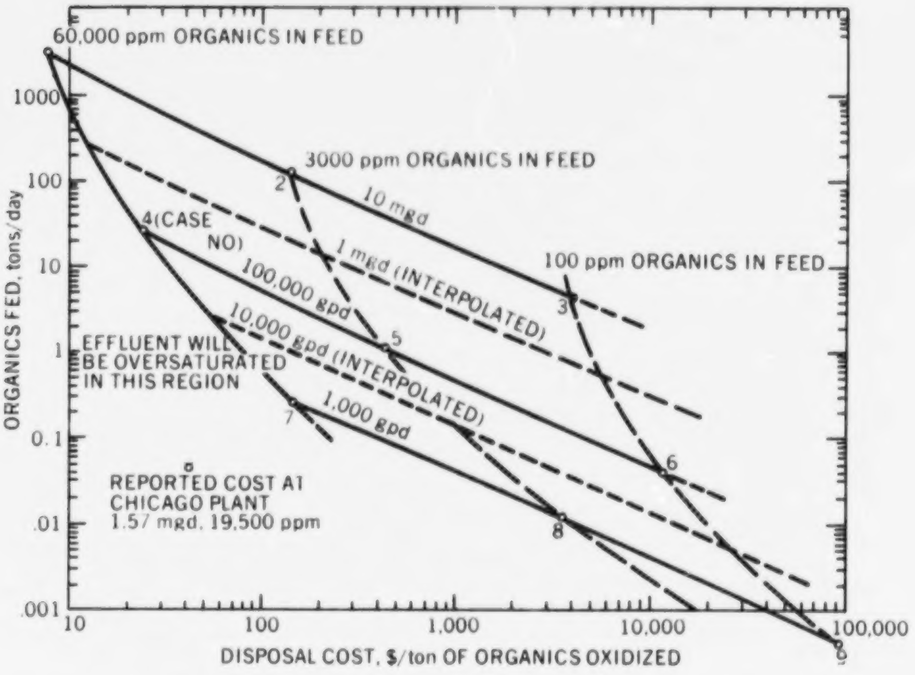


Figure 46. Ultimate disposal by wet oxidation: disposal costs for weight of organics oxidized.

capacities studied, that is, from 1,000 gpd to 10 mgd of concentrated wastes. These costs are compared with those for other processes in Table 8. In Figure 46, disposal costs, adjusted to a Marshall and Stevens Chemical Process Equipment Cost Index of 240, are presented in terms of the weight of organics oxidized.

Table 8. ULTIMATE DISPOSAL OF CONCENTRATED WASTES: COMPARATIVE PLANT COSTS AND PROCESSING COSTS FOR DIFFERENT DISPOSAL METHODS

Process	Capacity of disposal plant, mgd	Plant costs per gpd capacity, $	Disposal costs per 1,000 gal. waste liquor, $	Process effective on:
Wet oxidation	10	4.00	1.40	Organics only
	0.001	80.00	35.00	
Incineration	10	9.62	5.08	All combustibles
	0.001	97.80	55.10	
Injection to porous underground formations	2	-	0.12	Total waste stream
	0.1	-	4.50	
	0.001	-	27.00	
Placement in underground cavities	10	-	72.00[a] 0.27[b]	Total waste stream
	0.1	-	84.00[a] 2.70[b]	
	0.001	-	243.00[a] 139.00[b]	
Surface spreading	10	0.001	0.005[c]	Total waste stream
	0.001	0.22 (cost of land)	0.30[c]	

[a] Mined excavations.

[b] Nuclear-blast cavities.

[c] Infiltration rate: 0.4 ft/day.

In Figures 44 and 45 it is apparent that, as expected, wet oxidation plant costs and operating costs, on a unit flow basis, decrease as the capacity of the treatment plant becomes larger; however, it is significant (see Figure 46) that, for any fixed tons per day of organics, wet oxidation is cheaper if this fixed tonnage is contained in the smallest possible amount of feed liquor. In other words, the cost of disposal is less when a smaller quantity of concentrated waste is handled than when the same amount of organics is processed as a larger quantity of dilute waste. The 6 percent concentration limit still, however, applies.

Establishment of optimum concentrations of contaminants in the concentrated waste for processing by wet oxidation will be affected by both technical and economic considerations. For example, as has already been pointed out, oversaturation of the inorganic portion can limit the concentration of organics that can be handled under practical conditions. Cost relationships, as shown in the included cost curves, will also dictate the limitations under which wet oxidation can serve as a suitable ultimate disposal technique. In addition to these factors, ultimate disposal is irrevocably interrelated to the AWT process itself in such a way that the lowest cost for the total process of advanced waste treatment and ultimate disposal will finally determine the overall combination of treatment and disposal. A final answer to optimization of both processes must necessarily await the establishment of better cost data for the AWT processes themselves.

In the operation of an AWT process, a choice must be made between producing a relatively large quantity of low-concentration wastes or a smaller quantity of higher concentration wastes. The costs of ultimate disposal, when assessed against the volume of feed water recovered as product water, increase dramatically at relatively low product recovery ratios from the waste stream (see Table 9). From this interrelationship it is apparent that AWT processes must be carried on to comparatively high recovery efficiencies if a reasonable cost of ultimate disposal is to be achieved.

Table 9. COST, $/1,000 gal USABLE PRODUCT WATER, OF VARIOUS DISPOSAL METHODS[a]

Disposal method	Recovery of product water, %, and concentration of contaminants in waste, ppm, respectively.				
	99.90 300,000	99.83 180,000	96.67 9,000	80.00 1,500	50.00 600
Wet oxidation	---	0.015	0.091	0.538	---
Incineration	0.024	---	0.083 0.080[b]	0.240 0.192[b]	0.670 0.335[b]
Injection to porous underground formations	0.003	0.004	0.011	0.050	0.196
Placement in underground nuclear cavities	0.017	---	0.043	0.111	0.300
Pipeline conveyance to ocean:[c]					
1 mgd plant at 100 miles	0.032	0.045	0.220	0.700	1.480
10 mgd plant at 1,000 miles	0.115	0.150	0.760	2.340	4.900
100 mgd plant at 100 miles	0.004	0.005	0.027	0.060	0.086

[a] Based on 10 mgd inflow to AWT plant. Assumes 300 ppm total solids in feed — 100 ppm organics and 200 ppm inorganics.

[b] Total cost when pre-evaporation is employed to produce usable distilled water.

[c] Size of AWT plant and distance to ocean, respectively.

Wet oxidation shows considerable promise as a partial solution to the ultimate disposal of advanced treatment wastes, but, by itself, it is not a complete solution. Under practical operating conditions, wet oxidation will not achieve 100 percent oxidation of the liquid-borne organics. The supernatant liquors discharged from the process still contain, therefore, some organics that must be handled in some other way. Disposal of the inorganic materials must also be accomplished. The liquors discharged resemble the effluent liquor from the anaerobic digestion process and should respond to activated-sludge or trickling filter treatment. Although a portion of this liquor could be recycled to the secondary treatment unit for further biological oxidation, disposal of the entire volume by this method would contribute excessive amounts of inorganic material to the treatment plant and thence to the final effluent.

Further study will be needed to resolve the foregoing uncertainties regarding the suitability of wet oxidation as a method of accomplishing ultimate disposal of concentrated wastes.

INCINERATION

Incineration has been used as an effective method of disposing solids contained in sludge produced from various conventional sewage treatment processes by oxidizing most of the organic residues to innocuous H_2O and CO_2, leaving mostly noncombustible ash, a portion of which is water soluble.

In view of the similarity between aqueous sludges from conventional treatment processes and the concentrated wastes produced by AWT processes, incineration appears to be a good prospect for converting AWT wastes to an innocuous form. While incineration does not, by itself, accomplish "ultimate disposal" insofar as providing a final disposition of the total waste, it does, nevertheless, accomplish a relatively complete destruction of organic and other combustible components while simultaneously reducing the waste stream to substantially organic-free dry solids that are easily handled.

A preliminary process design and cost estimate have been made as a first step in evaluating incineration as a possible waste disposal technique. The evaluation includes estimated costs of disposing of the solid ash by hauling it to the seacoast for dumping into the ocean. For comparison, the contaminant concentrations and daily volumes of waste to be processed were the same as those selected in evaluating the wet oxidation process, namely, total contaminants (organic and inorganic) of 300, 000, 9, 000, and 300 ppm, and daily treatment volumes of 1,000, 100, 000, and 10 million gpd.

Types of Incineration Processes Considered

The Atomized Suspension Technique. Developed by the Pulp and Paper Research Institute of Canada, the Atomized Suspension Technique (AST) was considered for this application, but a detailed cost estimate was not made for a number of reasons. Previous investigators reported that efforts to adapt this process to the conversion of saline water and inland brackish waters demonstrated that dissolved solids contained in the waste liquor form deposits on the inside walls of the reactor, which reduces heat transfer efficiency. It was also felt that the AST process did not offer any substantial advantages over the multiple hearth — flash dryer system to be discussed later.

Box furnace process. Consideration was given to the possibility of spraying the liquid wastes into a conventional box furnace having a fire-brick lining and fired by oil, gas, or powdered coal, which would evaporate the water and oxidize the organics in a single chamber. Although this would appear to be the simplest method to use, several problems must be resolved before the method can be realistically proposed. For example, only fragmentary data are available on temperature and residence time required for complete oxidation of organics; air pollution control devices would probably be required to prevent atmospheric pollution by the stack gases, but to resolve this question, more data are needed on the combustion products formed; and third, little is known about measures needed to prevent accumulation of solid residues on the inside of the furnace walls.

Calcination processes. A number of processes that have been studied in atomic energy work for reduction of processing wastes to dry solids by calcination have been considered. These include Fused-Salt Calcination, the Rotary Ball Kiln, and Fluidized-Bed Calcination. These processes, operating at temperatures ranging from 350°C to 700°C, while suitable for the disposal of relatively small quantities of nuclear wastes, were rejected for this application because of their comparatively high cost of operation, the inadequate design data on which to make satisfactory cost estimates, and the difficulties involved in handling the fused salts they produce.

Flash dryer and multiple-hearth furnace. The combination of a flash dryer and a multiple-hearth furnace was selected as the most suitable incineration system for this application because of its adaptability to the drying and incinerating of wet-sludge-type materials. A schematic arrangement of this combination process is shown in Figure 47. Hot combustion gases from the gas-, oil-, or coal-fired multiple-hearth furnace pass up the stack, moving countercurrently to the sludge, which drops down the stack. Drying occurs in this flash drying zone and the solids then drop onto hearths inside the furnace where the combustibles are burned by the high temperatures produced by the conventional fuels. Dry solids carried up the stack by the flow of combustion gases are cyclone separated and then mixed with the inflowing waste to increase the solids content of the 30 percent solids feed stream. This creates a drier sludge that is easier to feed to the flash dryer system.

Investment and operating costs were estimated for this design over the range from 412 to 4,120,000 pounds per hour of feed liquor containing 30 percent solids, these weights corresponding to capacity ranges from 1,000 gpd to 10 mgd of the greatly concentrated wastes. Cost estimates for the less concentrated wastes included separate pre-evaporation to 30 percent solids since concentration of the waste in evaporators was found to be less expensive than evaporation in the incinerator. It was felt that concentration to 30 percent solids was about as much as could be obtained efficiently in an evaporator.

In the pre-evaporation of less concentrated wastes, additional usable product water may result. This could reduce the costs chargeable to the disposal process. The effect of this concentrating step on disposal costs because of water produced is shown in Table 9.

As with wet oxidation, incinerator plant investment costs per unit of waste flow treated decrease substantially for larger capacity plants. As shown in Table 8, incinerator plant costs per gpd of incinerator feed range from $9.60 at 10 mgd to $98 at 1,000 gpd, and the cost of treating wastes, in dollars per 1,000 gallons of incinerator feed, ranges from $5.10 to $55 for corresponding capacities.

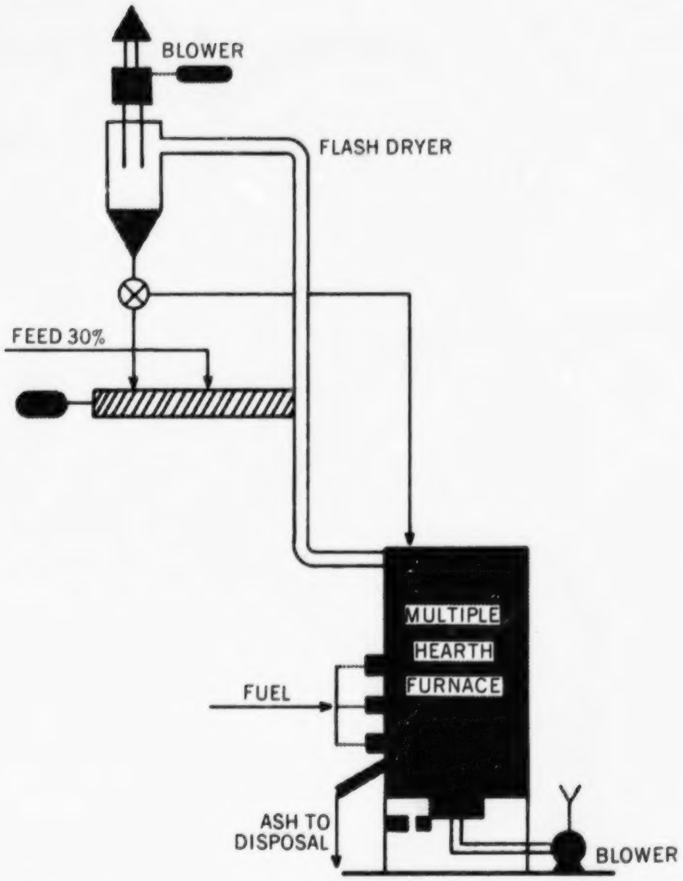


Figure 47. Ultimate disposal by incineration: Schematic arrangement of multiple-hearth and flash dryer. Equipment dries and burns concentrated wastes, leaving only a dry ash.

Although the total cost of waste disposal by incineration will be somewhat affected by hauling distance if the dry-solid residues are disposed by dumping in the ocean, the hauling cost becomes a negligible part of the total cost except when it involves greatly concentrated wastes. A comparison of unit disposal costs as affected by concentration and hauling distance is shown in Figure 48.

The degree of recovery of product water in the AWT plant has a profound effect on the cost of disposal. Obviously, the greater the product recovery, the less total volume of waste will remain to be disposed. The relation of costs of the disposal process to the cost of usable water produced for different recovery ratios is shown in Table 9 with a 10-mgd flow to the AWT plant as an example.

Incineration has much promise as a solution to the ultimate disposal of advanced treatment wastes. Although not quite a complete disposal technique, it goes further than wet oxidation and leaves only a dry organic-free ash to be disposed beyond the incineration process itself.

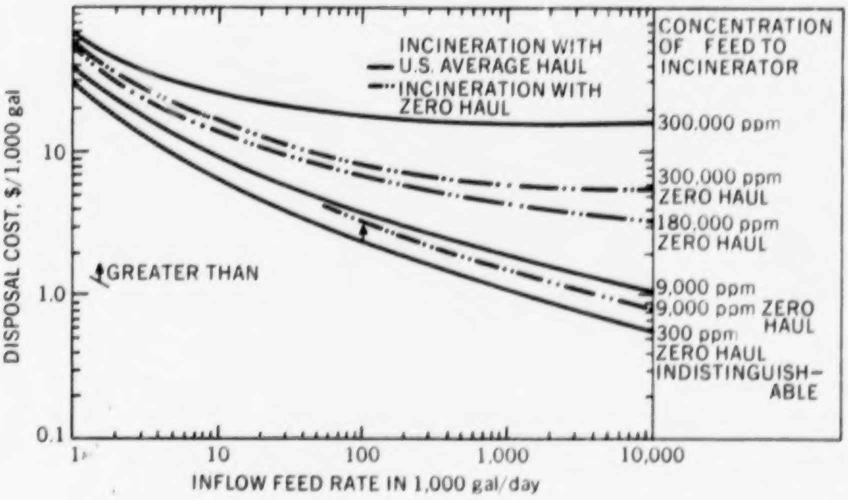


Figure 48. Ultimate disposal by incineration: Disposal costs per volume of processed waste as related to size of incineration plant.

It is anticipated that incineration will be further investigated, to obtain experimental confirmation of many of the assumptions necessarily made for the cost comparisons presented here and to establish definitely the technical feasibility of the process.

INJECTION TO POROUS UNDERGROUND FORMATIONS

Measured by everyday standards, the pore volume of storage space available under ground is enormous. A porous stratum of the type suitable for an underground reservoir can be expected to have a porosity of 25 percent. As an example of the storage capacity available in such a formation, it would be possible to pump 20,000 gallons of liquid per day for 100 years before filling the space available in a 20-foot-high cylinder to a radius of 2-1/2 miles. Even a flow of 2 mgd, forced into the same 20-foot-high cylinder for 100 years, would extend out only 4.75 miles from the point of injection. From computations such as these it seems fair to conclude that under reasonable conditions one may anticipate that injection could be practiced into the far future insofar as underground pore volume capacity is concerned.

In considering injection to underground formations as a method of ultimate disposal for concentrated wastes from advanced treatment processes, the possibility of contaminating existing ground water supplies must be investigated. For this reason, only formations that are completely isolated from usable underground streams could prove acceptable as waste disposal reservoirs. This essentially limits the injection approach to comparatively deep wells and to formations not connected by faults or other geologic structures to water-bearing strata.

The extensive experience gained by the oil industry in the drilling of gas and oil wells and in the reinjection of salt water to oil formations provides a wealth of geologic and technological data on which to base cost estimates for drilling and pumping, and serves as a guide in establishing the feasibility of various aspects of the proposed disposal method. The know-how of deep-well drilling and the geological information available on porosity, origin, and composition of underground formations will be directly applicable to many aspects of a deep-well-injection waste disposal approach.

Waste disposal by injection would involve (1) drilling deep wells up to 15,000 feet, (2) lining the hole with conventional oil well casing, (3) cementing the casing to prevent leakage to the surface or to intercepted underground water strata, and (4) providing a pressure pumping system capable of developing pressures in excess of 900 psi. A schematic arrangement for this type of disposal system is shown in Figure 49.

As has been previously reported, preliminary process designs and cost estimates for waste disposal by injection have been based on concentrated waste flows of 1, 000 gpd, 100, 000 gpd, and 2 mgd at total contaminant (organic and inorganic) loadings of 300, 9,000, and 300,000 ppm respectively. The evaluation was made for well depths of 3, 000, 7, 000, and 12, 000 feet and for wellhead pressures of 0, 260, and 900 psi. To stay within limits of conventional drilling equipment and standard sizes of oil well casings, the size of individual injection wells is presently limited to a capacity of 2 mgd. Capacities beyond this point can be achieved by replication. Based on 14 components of injection well costs analyzed in this study, economic diameters have been established at the various capabilities, depths, concentrations, and pressures selected for analysis. These were 8-5/8- to 10-3/4-inch casings for the 2-mgd wells, 2-7/8- to 4-1/2-inch casings for the 100,000-gpd wells, and 2-7/8-inch casing for the 1,000-gpd wells.

Because of extreme variations in the composition of the concentrated wastes and the variable nature of the underground formations receiving the waste stream, any incompatibility between these two materials may possibly incite a chemical reaction or a change of state that could produce a cementing agent or a precipitate, either of which could act to plug the porous strata. To avoid such a predicament, pretreatment of the waste stream to render it compatible with the underground receptor is considered a prerequisite to the injection process, and some allowance has been included in the cost analysis for this eventuality.

Costs of injecting wastes to various depths underground are shown in Figure 50 for the three flows studied: 1, 000 gpd, 100, 000 gpd, and 2 mgd at the operating pressures selected; the curves cover well depths ranging from 2, 000 to 13, 000 feet and include investment charges in addition to the estimated expense of preconditioning the waste stream. The capacity of the process was evidently the strongest determinant affecting cost per 1, 000 gallons of waste injected, unit disposal costs being significantly lower at the larger capacities (10 mgd) than at the

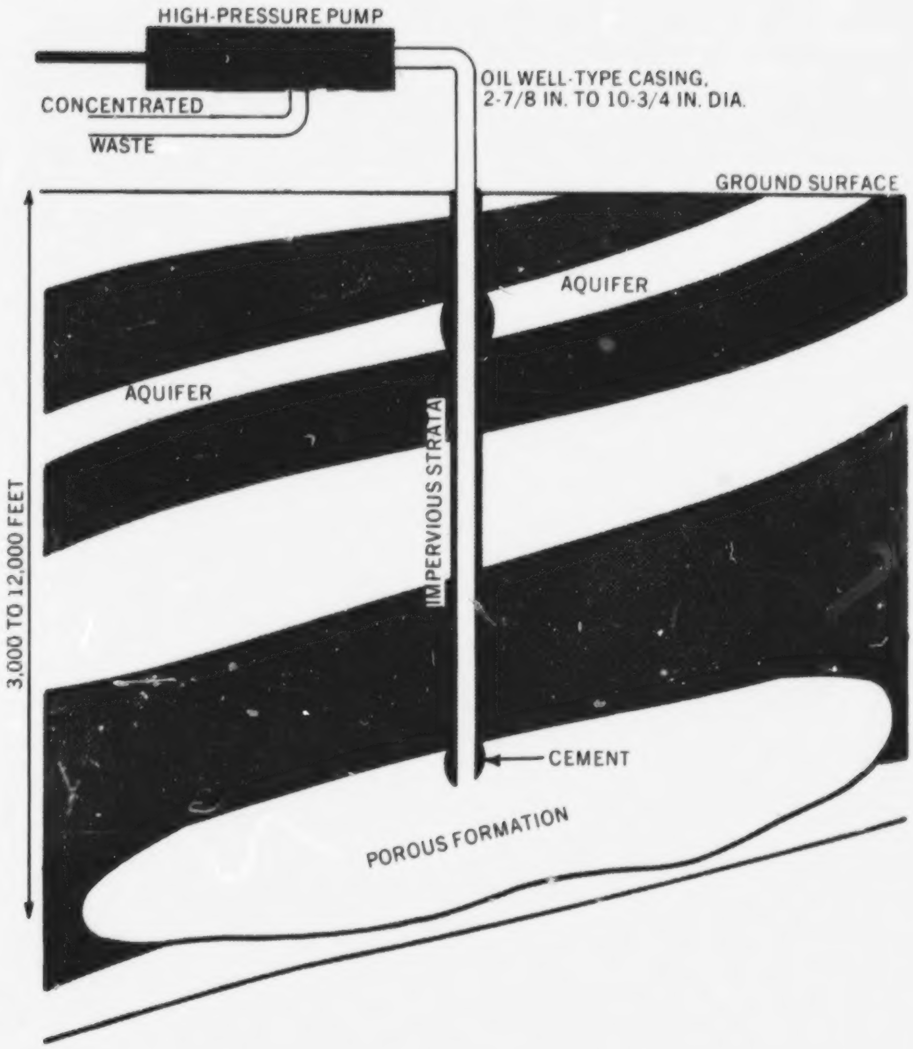

HIGH-PRESSURE PUMP
CONCENTRATED
WASTE
OIL WELL-TYPE CASING,
2-7/8 IN. TO 10-3/4 IN. DIA.
GROUND SURFACE
AQUIFER
AQUIFER
IMPERVIOUS STRATA
3,000 TO 12,000 FEET
CEMENT
POROUS FORMATION

Figure 49. Ultimate waste disposal by injection to underground porous formations. Storage space available in porous underground formations is enormous and could accommodate very large waste flows for many years. The liquid wastes are forced into these formations by high-pressure pumps. Formations used must be located from 3,000 to 12,000 feet below ground surface to guard against leakage into water-bearing strata.

smaller capacities (1,000 gpd) evaluated. This relationship is illustrated further in Figure 51, giving unit disposal costs for three cases of well depths in relation to total daily injection volume. For average values of well depth (7,000 ft) and injection pressure (260 psi), injection disposal costs would amount to about 12 cents, $4.50, and $27 per 1,000 gallons of concentrated wastes injected at capacities of 2.0 mgd, 100,000 gpd, and 1,000 gpd, respectively. Note (Table 8) that projected costs for the injection method of disposal are somewhat lower than previously reported costs for wet oxidation and incineration. Cost of conveyance to the well would be in addition to the above figures.

With the hypothetical case of a 10-mgd AWT plant for comparison, injection disposal costs per 1,000 gallons of product water produced amount to only 1 cent and 5 cents for recovery efficiencies of 96.67 and 80 percent respectively. These costs are also appreciably lower than comparable costs for either wet oxidation or incineration. Additional comparisons between these and other recovery ratios are given in Table 9.

Injection of concentrated wastes to porous underground formations appears to offer both a practical and an economical method of disposing the residues produced by AWT processes. A major advantage of this disposal method is the fact that the total waste stream is dealt with, leaving nothing that requires further handling. The increasing use of injection wells by industry for disposing organic and inorganic wastes lends considerable support to the technical feasibility of this disposal method. A recent review[24] by the U. S. Bureau of Mines covering sub-

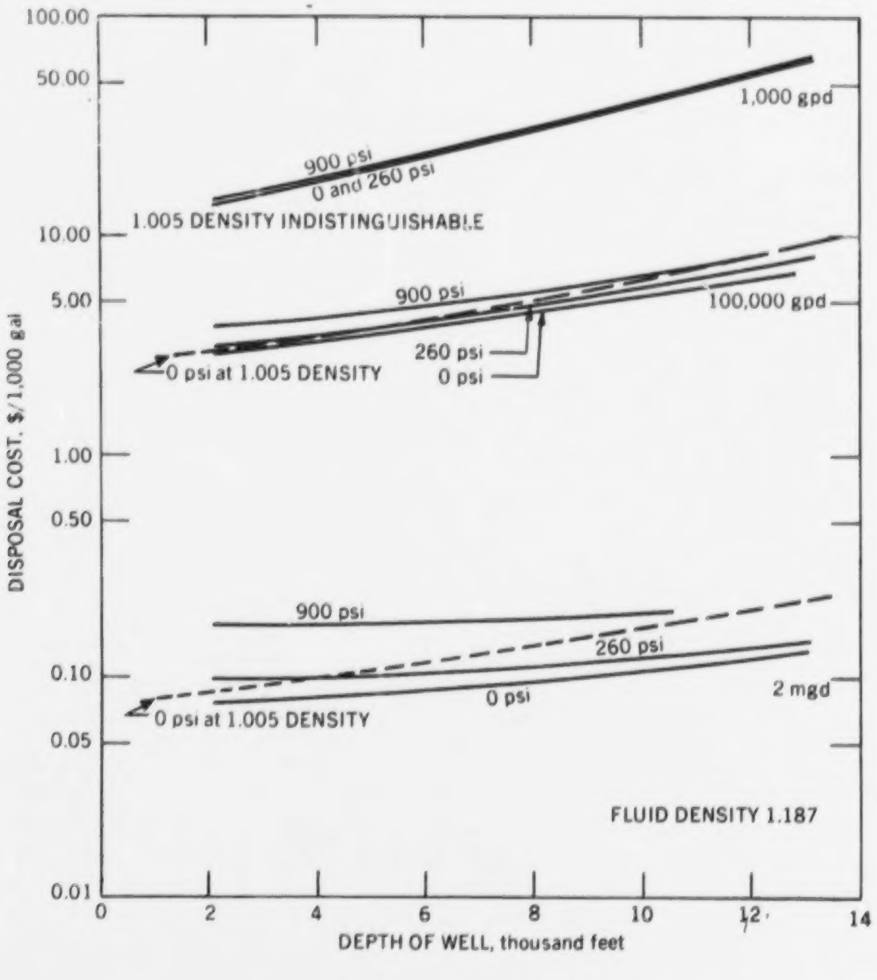


Figure 50. Ultimate disposal by injection to underground porous formations. Disposal costs (include conditioning and injection) per volume of injected waste as related to depth of well.

surface disposal of industrial wastes in the United States reports on 30 successful industrial-waste installations employing injection wells ranging from 300 to 12, 000 feet in depth.

A continuing effort by the AWTR Program will be directed to the further development of the injection disposal technique. A current project involves a compilation of geological data to assemble information regarding the type, extent, and geographical location of underground porous formations throughout the United States.

PLACEMENT IN UNDERGROUND CAVITIES

Underground storage is becoming an acceptable industrial practice, the primary use so far being for the storage of liquified hydrocarbon fuels. In 1956 there were 244 industrial cavities in use, all but 10 of them mined in salt formations. By 1960 there were 29 mined cavities in rock formations other than salt. Their success is based largely on the fact that for the materials stored, such as liquified petroleum gases, the cost of aboveground storage is much greater than the cost for underground storage.

A preliminary evaluation has been made of the technical and economic feasibility of employing underground cavities as permanent storage sites for concentrated wastes from AWT processes. A listing of the possible types of cavities that might be suitable for liquid-waste storage includes:

1. Natural underground cavities.

2. Existing man-made cavities--abandoned or depleted mines, oil wells, or gas wells.

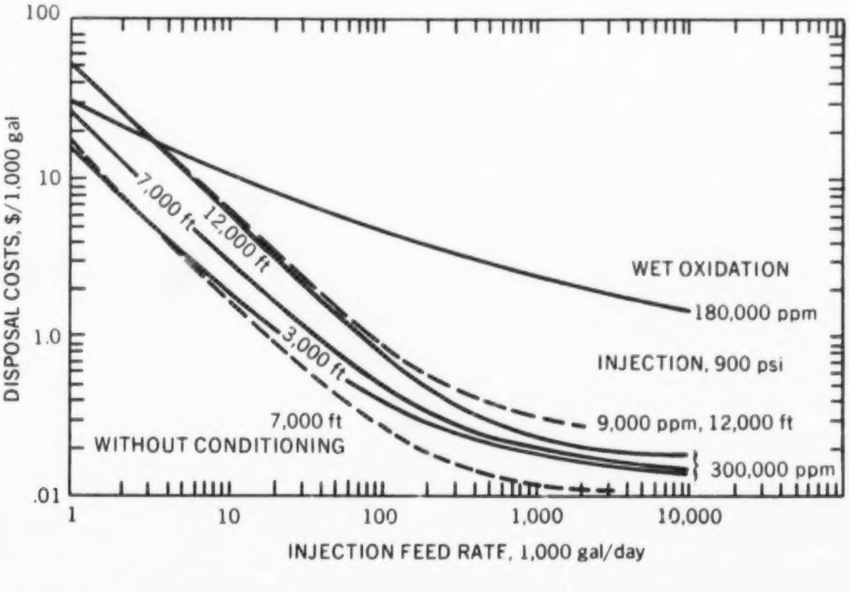


Figure 51. Ultimate disposal by injection to underground porous formations. Unit disposal costs per volume of injected waste as related to daily volume of waste injected.

3. Salt cavities--developed for waste disposal by mining or dissolving salt.

4. Mined cavities--constructed specifically for waste disposal usage.

5. Nuclear blast cavities--created specifically for waste disposal usage.

Natural Underground Cavities

Natural underground cavities have some potential as waste disposal sites but there is inadequate information on their extent, geographical occurrence, and general suitability for this purpose. Natural cavities could prove suitable in certain local situations, but they do not occur extensively enough to be considered a dependable solution for nationwide application. Their general occurrence in limestone formations, often at very shallow depths, increases the possibilities of ground-water contamination and is a deterrent to their use for waste disposal.

Existing Cavities--Abandoned or Depleted Mines, Oil Wells, or Gas Wells

In considering the possibility of using existing underground cavities, it is only natural to look to abandoned and depleted coal and mineral mines (Figure 52) as well as exhausted oil wells and gas wells. Although an extensive feasibility study has not yet been made, the use of existing cavities has a number of severe limitations that, taken together, make the procedure very questionable as a general solution. In the case of mines, particularly bituminous coal mines, many of which intercept ground water strata, effective sealing of cracks and crevices to prevent seepage of the disposed wastes into underground streams would be an extremely difficult and unreliable undertaking. A further problem relates to the question of when a mine becomes depleted. Changing technology in the past has often made possible the conversion of a presumably worthless mine or depleted oil well into a producing property. This point has been emphasized in preliminary studies on the proposed disposal of radioactive wastes by injecting them into depleted oil and gas fields. The petroleum industry has stated that determining when an oil or gas field is actually depleted is difficult.

While a lengthy specialized study would be needed to determine the available volume of existing cavities, preliminary investigation has disclosed that underground mining in the U. S. creates 150 mgd of cavity space of which 76 percent (116 mgd) results from bituminous coal mining (including strip mining). Further study and investigation are needed (1) to locate these cavities, (2) to determine what portion of them might become suitable for storage of wastes, and (3) to determine their individual suitability for use in ultimate disposal. Although the greatest potentialities exist in bituminous coal cavities,

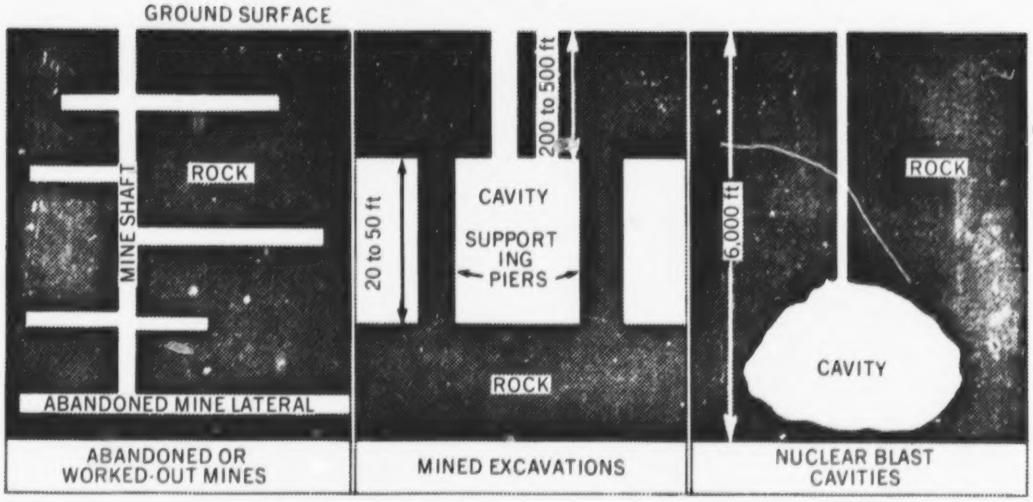


Figure 52. Ultimate disposal by placement in underground cavities. Three types of cavities that could be suitable as permanent storage basins for concentrated wastes from advanced waste treatment processes.

since their distribution follows somewhat the national distribution of waste production, the prospects for their suitability are not particularly outstanding.

Over 80 percent of the cavity volume created by current mining operations occurs as surface mining. Except where these excavations occur in remote and isolated areas, disposal of wastes in surface cavities would almost automatically involve contamination of ground water if not of surface waters. Further, they could create hazards and nuisances by their existence.

Salt Cavities

Salt cavities provide the major method of creating underground storage space for present industrial use. Caverns in salt formations can be developed through solution mining or by conventional mining methods. In either case, disposal of the salt removed must be accomplished with the same regard for preventing pollution of existing water supplies as disposal of the advanced treatment wastes themselves. From a study of the mining and spoil disposal aspects of this proposal, the difficulties and expenses of disposing the salt waste produced from the cavity were demonstrated, under all conditions evaluated, to be greater than those for disposing the advanced treatment waste itself. Ultimate disposal to salt cavities, in which salt was mined solely to create storage space for advanced treatment wastes, would, therefore, be an impractical solution. The emphasis upon salt cavity storage for radioactive wastes cannot be translated into optimism for the disposal of advanced treatment wastes because the problems differ in a number of parameters by several orders of magnitude.

Mined Cavities

Costs have been calculated for cavities mined for the sole purpose of providing storage space for advanced treatment wastes. Optimum sized caverns for each of the waste-flow capacities studied were determined on the basis of an economic evaluation that considered investment required for the excavation, interest, taxes, and insurance, but did not include the cost of hauling spoil material, nor the rental cost of the dump land, both of which would be of little consequence to the total cost. Optimum sizes for the 1,000- and 100,000-gpd waste flows would involve caverns that would be filled in 14 years and 2 years respectively. A 1-year economic life (filling time) was selected for the 10-mgd flow, though this size was based on practical rather than optimum economic considerations. Disposal costs for mined caverns would amount to \$243, \$84, and \$72 per 1, 000 gallons, respectively, for concentrated waste flows of 0. 001, 0. 1, and 10 mgd. These costs, even at the 10-mgd capacity, are extremely high by comparison with other methods of disposal (see Table 8). On the basis of these costs, mined caverns, constructed solely as waste disposal receptors, are not considered to be economically feasible for ultimate disposal.

Nuclear Blast Cavities

Use of nuclear devices to create underground waste disposal caverns is a distinct possibility that may find future application. Some costs have been developed for this method but must be considered highly speculative because of the scanty data available on underground nuclear explosions and the high scale-up factors from experimental explosions. Serious consideration has, however, been given to this approach because the preliminary disposal cost estimates are very low and compare favorably with other methods proposed. Disposal costs for nuclear cavities approach the cost of injection as very high capabilities and remain superior to wet oxidation and incineration at intermediate capabilities. For 0.001-, 0.1-, and 10-mgd waste flows, the costs amount to \$140, \$2. 70, and \$0. 27, respectively, per 1, 000 gallons of concentrated waste disposed (Table 8). Based on the example of a 10-mgd AWT plant, the cost of disposal to nuclear cavities per 1, 000 gallons of product water recovered amounts to 11 cents, 4. 3 cents, and 1. 7 cents at recovery ratios of 80, 96. 67, and 99. 9 percent respectively (Table 9).

Summary

With the exception of certain shallow cavities from which contamination of ground waters might occur, the use of underground cavities for ultimate disposal of concentrated wastes is considered technically feasible. Excavation of salt cavities for disposal purposes is, however, impractical because of the waste salt disposal problems. Although the cost of very large nuclear cavities is comparatively low, the construction of these cavities, particularly near populated areas, is a highly speculative undertaking at this time. For very small daily rates (1, 000 gpd), disposal to conventional mined cavities approaches the cost of disposal to nuclear cavities (Figure 53). At increasing daily flow rates, however, the unit cost for nuclear cavities falls off very rapidly whereas that for conventional mined cavities remains constant. Thus, with the reservation that estimates for larger nuclear cavities involved a relatively high degree of speculation and high scale-up from present knowledge, it may be concluded that larger conventionally mined cavities are well out of the running compared with nuclear cavities.

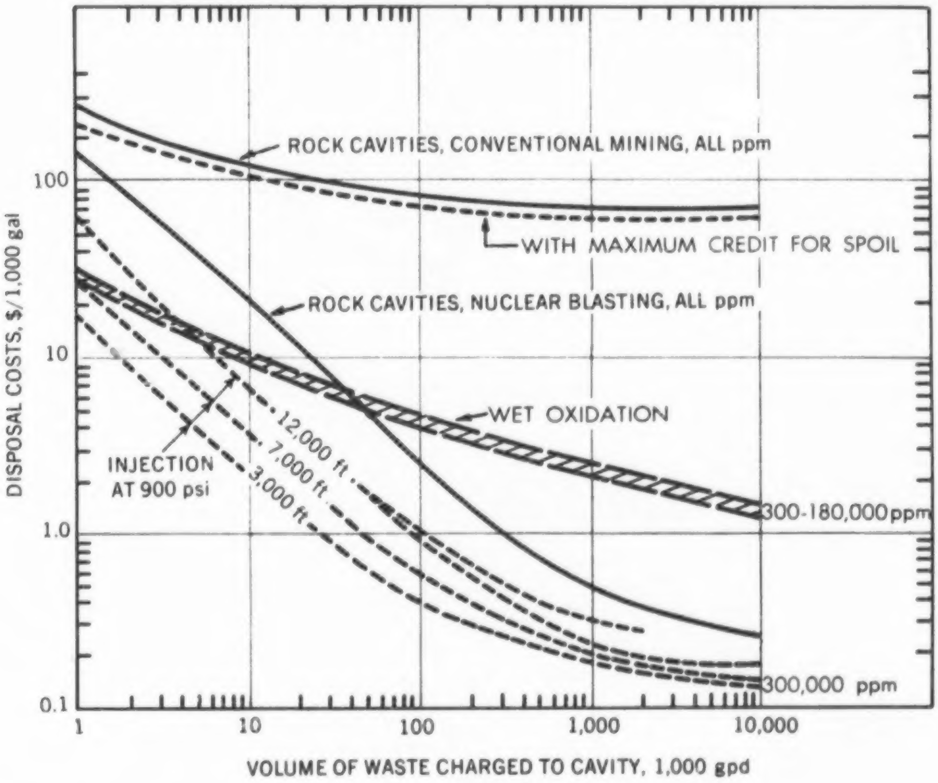


Figure 53. Ultimate disposal by placement in underground cavities. Disposal costs for mined cavities and nuclear-blasted cavities compared with costs of wet oxidation and injection to porous underground formations.

SPREADING

Spreading refers to the practice of spreading liquids on the ground surface to induce their infiltration into the ground. This is ordinarily accomplished by ponding the waters but may sometimes be achieved by sprinkling with irrigation sprinklers. Spreading is an accepted method of intentionally recharging waters to underground aquifers for future withdrawal and use. The rather extensive recharge occurring as an incidental consequence of irrigation further supplements deliberate recharge by spreading and natural ground-water replenishment from rainfall and natural drainage. Although most deliberate recharging involves excess surface runoff, the reclamation of both primary and secondary sewage effluents by spreading has been extensively practiced though somewhat less extensively studied.

Secondary waste treatment plant effluents with relatively small contaminant loadings will, in many instances, be acceptable for ground-water recharge. The concentrated wastes anticipated as end products from AWT processes will not, however, be suitable under any circumstances for ground-water recharge purposes when the recharge implies eventual re-use of the ground water, even though extensive purification may occur when contaminated water seeps into and through the soil. Biodegradable organics and microorganisms are often effectively removed, but essentially no removal of dissolved inorganics occurs.

In proposing the spreading technique as a method of ultimate disposal for advanced treatment wastes, there would be no intention of returning these concentrated wastes to a ground-water aquifer serving as part of a water supply. Spreading is, therefore, applicable as an ultimate disposal method only in areas where there will be no future use of the ground water or where the aquifer is already written off as a resource because of excessive pollution. This generally limits the applicability of spreading for ultimate waste disposal purposes to desert basin areas hydrologically enclosed.

The practice is, nevertheless, of more than passing interest because, as mentioned above, spreading of secondary treatment plant effluents with relatively low dissolved-solids contents will find acceptable applications in areas where existing ground waters can tolerate whatever pollutant load is involved. Although this use of spreading does not achieve true ultimate disposal, it does, in effect, achieve tertiary treatment while eliminating or postponing the need for ultimate disposal in instances where it is applicable.

In evaluating the feasibility of the spreading technique, a preliminary process design and cost estimate were made for the range of waste flows previously studied, namely, 0.001, 0.1, and 10 mgd. The concentration of contaminants was considered not to be a parameter in spreading. Infiltration rate and cost of the land were the other independent parameters evaluated. The infiltration rates used were 0.4, 1.0, and 4.0 feet per day, and land costs were \$25, \$50, and \$1,000 per acre. The evaluation was based on the assumed use of shallow square ponds formed by a series of dikes to serve as infiltration basins.

As developed in this study, the costs for spreading are only one one-hundredth or less of the comparable costs for other disposal methods studied (Figure 54). These ranged from 30 cents per 1,000 gallons of water spread at the 1,000-gpd flow rate and 0.4 foot per day infiltration rate to around 0.1 cent per 1,000 gallons of water spread at 10 mgd and 4.0 feet per day infiltration rate (Table 8 and Figure 55). These unusually low estimated costs are, however, based on the assumption that spreading would take place immediately adjacent to the treatment plant; conveyance of the waste stream for even a short distance from the plant to the spreading grounds would, therefore, immediately detract from the low-cost advantage for spreading. Unit disposal costs are only slightly higher when spreading is done on $1, 000-per-acre land, for comparable flow rates, then when carried out on $25-per-acre land, emphasizing that, contrary to expectations, expensive land is not particularly a deterrent to use of the spreading technique. This is occasioned by the disclosure that cost of land is not a major expense in the overall construction and operation of spreading basins.

Water spreading will apparently have, therefore, some general application within the overall boundaries of the AWT concept, but its applicability as an ultimate disposal technique is essentially limited to

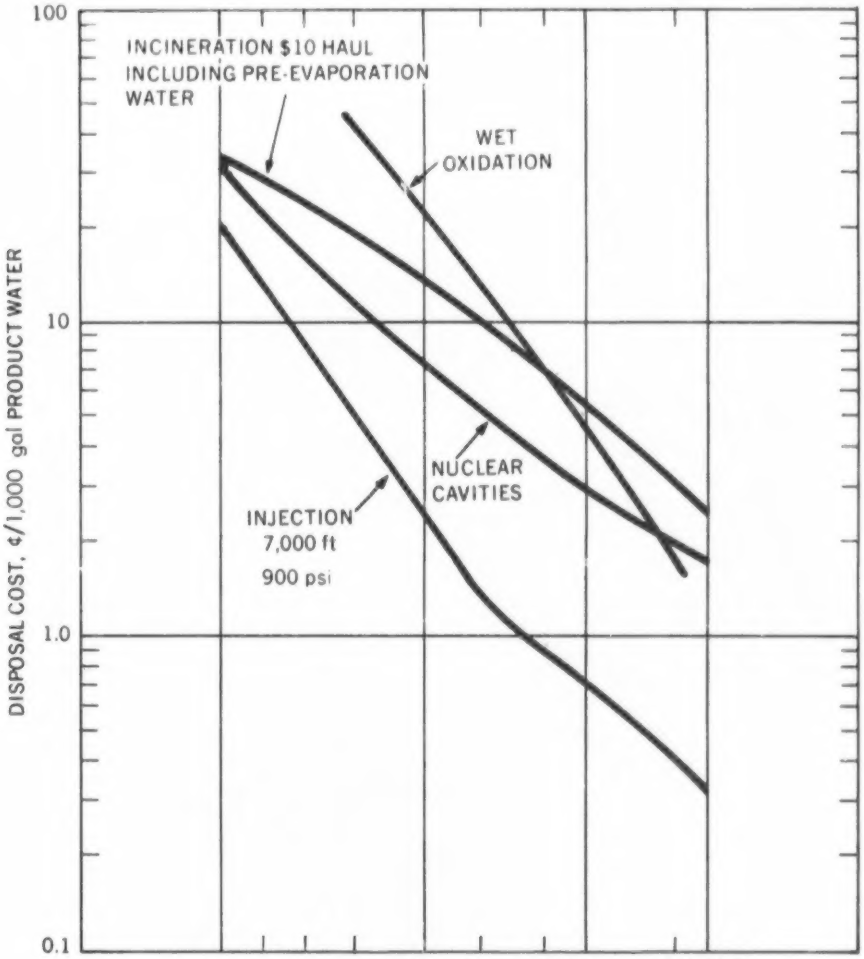


Figure 54. Ultimate disposal of advanced treatment wastes: Comparison of costs for different waste disposal methods according to recovery efficiency in advanced treatment plant (based on a 10 mgd secondary effluent with 300 ppm total contaminants).

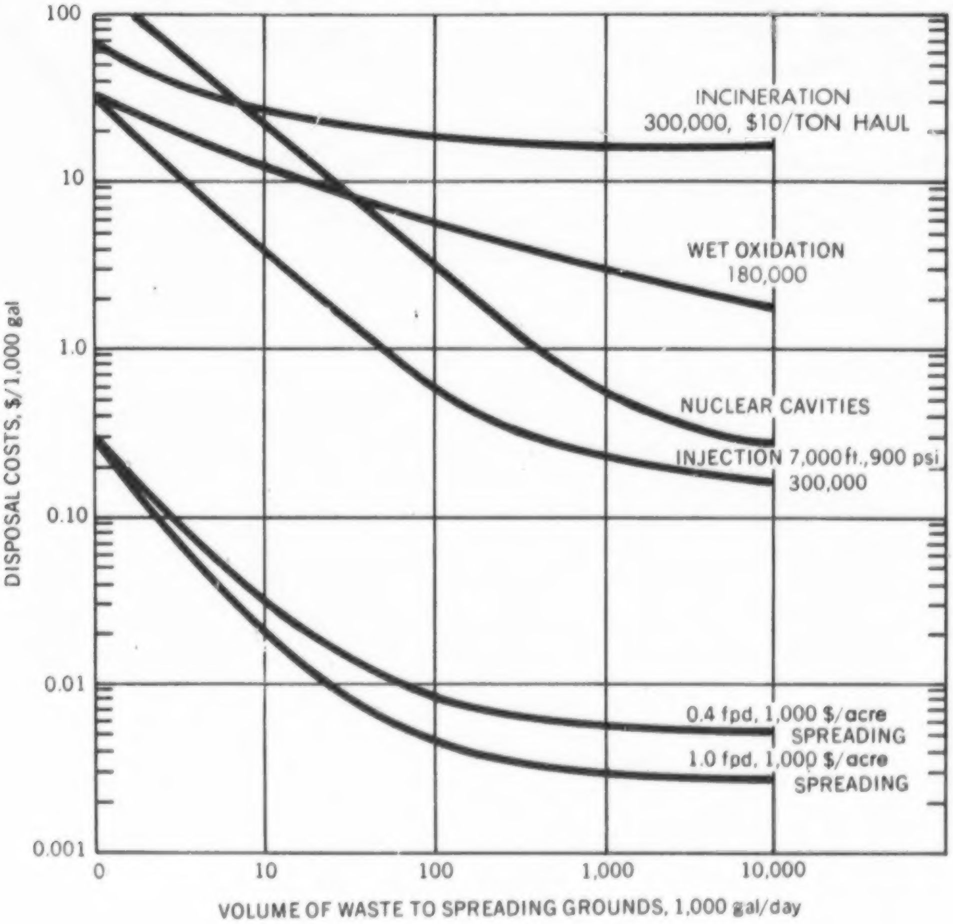


Figure 55. Ultimate disposal by spreading: Disposal costs as related to daily volume of waste handled.

the uninhabited and uninhabitable areas of this country. Clearly, these are exactly the areas having the least need for advanced treatment. On the other hand, where communities have developed in these desert areas, the need for advanced treatment is intense, and ultimate disposal by spreading in nearby hydrologically closed basins may very likely be practicable for these communities.

PIPELINE CONVEYANCE TO OCEAN

A pipeline system for conveying concentrated advanced treatment wastes from their point of origin to the ocean has many advantages as an ultimate disposal method. The diluting capacity of the ocean is so great that even the most concentrated wastes could be disposed without creating objectionable conditions, and this method would achieve truly ultimate disposal of the total waste stream. Furthermore, from knowledge gained by past experience in the pumping and conveying of liquids and slurries through pipelines, it is safe to conclude that such a method is 100 percent technically feasible without conducting extensive studies.

Such a disposal system for advanced treatment wastes would require a continuous pipeline, probably underground, with a series of pumps to move the liquid to an outfall extending as much as 30 miles out to sea. An alternative to the underwater outfall would be to barge the liquids to whatever distance from shore is necessary.

To determine the economic feasibility of such a proposal, a study was undertaken to obtain preliminary cost data for pipelining (1) under various conditions of product recovery from the AWT plant, (2) for various AWT plant capacities, and (3) at different distances inland from the seacoast. As shown by the map, Figure 56, no point in the United States is farther than 1,300 airline miles from the sea; hence, a pipeline conveyance system serving any community in the country would be within this distance range.

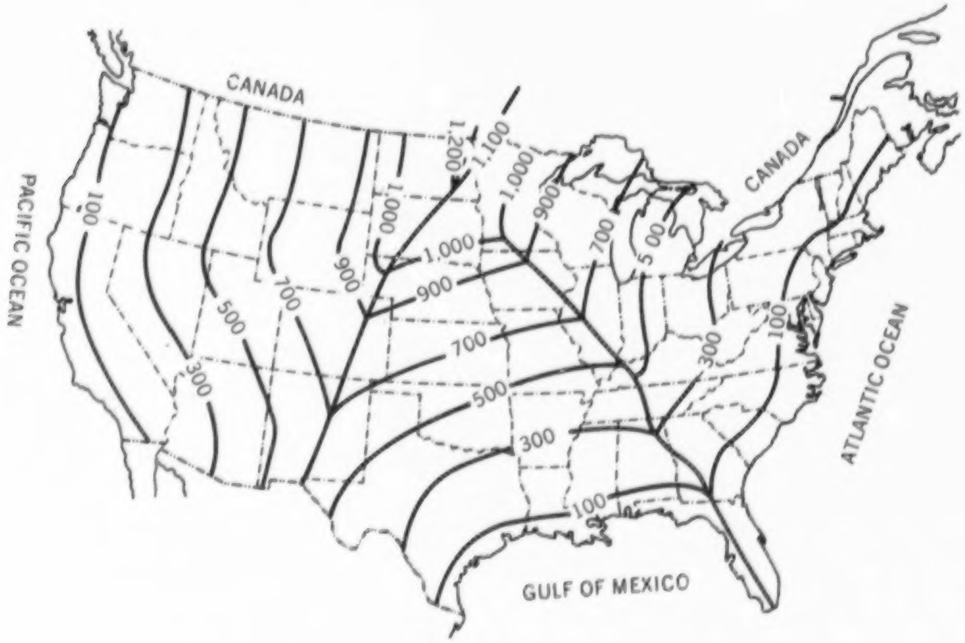


Figure 56. Ultimate disposal by pipeline conveyance to ocean. Airline miles from any point in the United States to the nearest ocean. These lines approximate pipeline distances that would be involved in the pipeline conveyance of wastes for disposal in the ocean.

Very preliminary costs were calculated for pipelining the residues for distances of 100, 500, 1,000, and 1,300 miles from AWT plants with capacities of 1, 10, and 100 mgd, on the assumption of recovery efficiencies ranging from 50 to 99.9 percent. The study showed that at high AWT capabilities (100 mgd) and recovery ratios of 99.9 percent, the unit disposal costs are unusually reasonable, ranging from 0.4 cent per 1,000 gallons of product water at the 100-mile transport distance, to 5 cents per 1,000 gallons of product water at the 1,300-mile distance. The costs increase rather sharply, however, with increasing transport distances and with lower recovery efficiencies. At 99.9 percent recovery, disposal costs amount to 32 cents per 1, 000 gallons of product water for a 1-mgd plant 1, 000 miles inland, increasing to $7. 00 per 1, 000 gallons of product water at 80 percent recovery for the same capacity and distance. Estimated costs for additional plant capacities, recovery ratios, and transport distances are reported in Table 9.

These projected costs are slightly on the low side since the calculations did not allow for the cost of dumping the waste after conveyance to the seacoast; this added cost will have only a negligible effect on transport distances over 100 miles. Moreover, the calculations were made by using the viscosity and density of water, and since the more concentrated wastes will have higher viscosities and densities, the true conveyance costs for concentrated wastes will be somewhat higher than shown here.

In addition to its favorable technical position, conveyance also looks attractive from the economic standpoint. There is still the possibility that use of pipelines designed to handle combined waste streams from two or more communities may result in an even more favorable economic situation by further reducing unit conveyance costs. On the other hand, however, a number of questions arise regarding certain nontechnical aspects of the conveyance disposal method. There are, for example, uncertainties about the distance beyond the coastline that would be required for dumping the wastes to satisfy all objecting interests. Complications could develop from international concern over discharging of wastes to the ocean, and the possible objections of conservationists and fishing interests concerned over the possible effects of wastes on flora and fauna of the ocean must be recognized.

Further studies will be needed to evaluate these and other aspects of the overall feasibility of waste disposal by conveyance to the ocean.

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APPENDIX A

APPENDIX A

CURRENT INTEREST IN AND PRACTICE OF WASTE-WATER RE-USE

Introduction

A waste-water renovation symposium, sponsored by the Public Health Service and held in Cincinnati, Ohio, on May 15 and 16, 1962, attracted 200 scientists including sanitary and chemical engineers, chemists, biologists, and representatives of several other related disciplines. Subsequent symposia on this subject have been sponsored by the American Chemical Society at their January 1963 meeting in Cincinnati, and by the American Institute of Chemical Engineers at their October 1963 meeting in San Juan, Puerto Rico. Both of these latter groups have scheduled additional seminars on water re-use in conjunction with their 1964 meetings.

As a part of their responsibility in evaluating the overall water supply needs of the Nation, the presidentially appointed Federal Water Pollution Control Advisory Board, known informally as "The President's Advisory Board," conducted public hearings on September 25, 1963, in Los Angeles relating to ground-water quality and waste-water reclamation in the southern California region. Almost without exception, every water resource authority testifying at these hearings commented on the necessity of taking a more realistic stand towards the use of waste waters, and on the need for accelerating the work required to convert municipal waste streams to usable water supplies. Mr. Frank G. Bonelli, Chairman of the Los Angeles Regional Water Pollution Control Board, stated, "Waste water reclamation, important to the whole Nation's future, has a greatly accentuated need in this [southern California] area, and the Board encourages it wherever waste water reclamation is compatible with beneficial uses of water." After considering testimony presented at this public forum and otherwise reviewing the water supply and pollution problems in the southern California area, the President's Advisory Board adopted a formal resolution recommending that "the Department of Health, Education, and Welfare be urged to expand its advanced waste treatment and waste water reclamation research and development program."

Further evidence of the increasing interest is contained in the agenda of the October 1963 meeting of the American Institute of Chemical Engineers, which included a symposium on waste-water renovation emphasizing the interdisciplinary aspects of the problem. Papers were presented by 10 recognized authorities on subjects ranging from the economic challenges involved to the microbiological and toxicological implications associated with the re-use of waste streams. The editors of Chemical Engineering Progress considered the discussions of sufficient importance and interest to feature the 10 reports in a 22-page coverage published in the November 1963 issue.

Featured as a lead article in the January 1963 issue of the Water Pollution Control Federation Journal was a comprehensive report entitled "Advanced Waste Treatment and Water Re-use" by Dr. Gordon E. McCallum, Chief of the Division of Water Supply and Pollution Control of the Public Health Service. He stated that the successful solution to the AWT problem "will require major effort by the best research and engineering minds in the country. The technology of advanced waste treatment must result from the combined effort of many disciplines -- sanitary engineering, chemical engineering, chemistry and the biosciences."

Although the direct re-use of treated waste waters in the United States is not yet widespread, recent years have seen a growing trend in this practice. Limited almost exclusively to the arid west and southwest, this usage has ordinarily been the outgrowth of serious water shortages or inadequate distribution facilities, both factors having caused water-short areas to take a second look at the disposition of their community waste streams. A major point in favor of the use of municipal waste effluents as sources of re-usable water is their ready availability in substantial and relatively consistent quantities. A number of communities have recognized and taken advantage of these factors.

Limitations in the types of usage to which only partially treated effluents can be put have resulted from the inability of conventional primary and secondary treatment processes to guarantee complete inactivation of potentially pathogenic organisms that could create a health hazard. To protect the public, State Health Departments have adopted regulations establishing limits of bacterial and viral counts, not only in domestic supplies, but also in waters used either for body contact sports or for irrigation of truck crops and other foods that may be consumed directly by humans. As a result of these restrictions, irrigation of agricultural crops such as alfalfa and cotton, and industrial cooling uses have become the principal applications of municipal effluents. Most streams destined for this re-use have had two-stage treatment plus chlorination.

AGRICULTURAL RE-USE

Irrigation of Crops

Cities may sell their treatment plant effluent to irrigate crops, public parks, or golf courses. One example of this practice is the Las Vegas, Nevada, sewage treatment plant, which supplies a single purchaser with irrigation water for 960 acres of alfalfa. More than one-fourth of Texas' 800 municipal sewage treatment plants provide effluents for irrigation of cotton or cattle feed crops. At Odessa, Texas, the city's waste stream undergoes primary sedimentation followed by stabilization pond treatment before being used to irrigate 60 acres of cotton and feed crops.

Irrigation of Public Parks and Golf Courses

Irrigation of golf courses has become a rather important use of reclaimed municipal effluent. In Prescott, Arizona, secondary effluent is slow sand filtered before it is used on the municipal golf course. Course fees are expected to pay for Prescott's entire park and recreational program if the city's present rate of growth continues. Other western communities irrigating golf courses with effluent include Jal, Carlsbad, Santa Fe, Los Alamos, and Gallup, New Mexico, and Winslow, Arizona.

At Sunnyside, Utah, public park lawns are irrigated with effluent that has been slow sand filtered and chlorinated. Treated effluent provides irrigation for lawns and shrubs in the Golden Gate Park in San Francisco, and the Flamingo Hotel in Las Vegas, Nevada, at one time used sand-filtered effluent for maintaining the hotel grounds.

INDUSTRIAL RE-USE

Use of municipal effluents for industrial process cooling is becoming more common in the western part of the country and is finding limited use in certain localities east of the Mississippi River. Municipal treatment plants at Odessa, Amarillo, and Big Spring, Texas, all sell effluent to industries. At Amarillo, a gasoline refinery and power plant purchase 5 mgd and pay approximately 10 cents per thousand gallons, while petroleum and chemical plants at Odessa use 3.5 mgd for cooling water. At Las Vegas, Nevada, the Nevada Power Company plans to use 2 mgd of effluent for cooling water in their steam-electric power plant. At Andrews, Texas, sand-filtered effluent is pumped into the ground for oil well flooding. In Burbank, California, a bond issue has recently been approved for the construction of a water reclamation plant to provide cooling water for the city's steam-electric generating station. At Sioux Falls, South Dakota, effluent discharged to the Big Sioux River serves as cooling water for a nearby nuclear-fuel power plant.

East of the Mississippi River, at Richmond, Indiana, an electric utility employs effluent from the Richmond Sanitary District for cooling water when flow in the White Water River drops. Bethlehem Steel Company's Sparrow Point Plant near Baltimore, Maryland, has used effluent from Baltimore's Back River Sewage Treatment Plant for cooling water since their former deep-well source became contaminated by salt-water intrusion.

RECREATIONAL RE-USE

Santee, California

The Santee Waste-Water Reclamation Project, situated 17 miles inland from the Pacific, near San Diego, California, has pioneered the direct re-use of reclaimed municipal waste water for recreational purposes. The major use of this water is for filling a series of manmade lakes open to the public for recreational uses. Initiated in 1959, this unique experimental project provides a recreational attraction for the 12, 500 area residents and has been enthusiastically accepted by the public despite their full knowledge of its sole source of water.

Four lakes have been created in a canyon of this arid area, the largest being 11 acres; two of these have been stocked with fish and landscaped; the development has created a habitat for waterfowl and other wildlife. Boating, picnicking, fishing, and an 18-hole golf course irrigated by the reclaimed water, are widely enjoyed by visitors. Initially the lakes were restricted to non-water contact uses, and fish had to be returned to the water. After completion of extensive microbiological studies, however, body contact sports are now permitted, and caught fish may be kept. After conventional primary and secondary treatment by activated sludge, the waste water from Santee begins its "advanced treatment" in a holding pond where the 30-day detention time permits additional oxidation. The water is then chlorinated and pumped to a spreading area where it is percolated into the ground; after flowing through sandy, rocky soil, it surfaces again and is fed into the recreational lakes. After passing through three recreation ponds, the renovated water overflows to form a stream used to irrigate an adjacent golf course.

Lancaster, California

Use of reclaimed domestic waste water for development of an inland aquatic park has been proposed at Lancaster, California, a community of 35, 000 situated on the edge of the arid Mojave Desert about 75 miles north of Los Angeles. The present treatment of the waste stream includes use of 240 acres of oxidation - evaporation ponds after primary sedimentation. Presently evaporated from the ponds or wasted to the desert, the 3 mgd flow would furnish water for three lakes totalling 19 acres of water surface to be used for boating and fishing. In addition, camping and picnicking facilities and a community club would be provided. Available water in excess of requirements would be used for irrigation of a regional park and golf course and for industrial purposes. Since the oxidation pond effluent is heavily laden with algae and algal nutrients, the success of this project will depend on the development of a tertiary treatment technique capable of removing algae from the pond effluent sufficiently for an acceptable appearance of the water, and algal nutrients to a level required to prevent regrowth of algae in objectionable concentrations. A research study is underway to investigate effective solutions to this problem. Possible approaches being considered include coagulation of the algae and nutrient compounds with subsequent removal by dissolved air flotation, or settling, followed by rapid-sand or other filtration techniques. The use of additional stabilization ponds in series to achieve lower algal densities and lower nutrient levels is being considered. Recovery of the algae for use as stock food is also receiving attention.

RE-USE FOR SALT WATER BARRIER

Santa Monica Bay Area

In some coastal regions where lowering of water tables has resulted in the intrusion of salt water to contaminate ground-water supplies normally pumped into municipal mains, there is a need for reinjection water to raise the water table and create a barrier against infiltration of sea water. Use of reclaimed waste waters to provide such a barrier in the Santa Monica Bay area has been studied by making experimental injections of highly treated effluent from Los Angeles' Hyperion Sewage Treatment Plant.

Treatment at Hyperion includes primary settling of raw wastes with secondary treatment by activated sludge. Effluent from these conventional processes destined for the pilot-scale injection study was given "advanced treatment" involving chemical coagulation and settling, sand filtration, and chlorination. This "polished" water was then pumped into a well discharging to the underground strata near the seacoast. Careful monitoring of the ground-water quality was done through a series of wells surrounding the injection well, and preliminary results of this experiment showed the water to be completely satisfactory for use in this type of application.

REPLENISHING GROUND-WATER SUPPLIES

Whittier Narrows Water Reclamation Plant

Use of renovated waste waters to replenish ground-water supplies depleted by excessive pumping has been practiced in Los Angeles County since August 1962. Planned, designed, and operated by the Los Angeles County Sanitation Districts, the Whittier Narrows Water Reclamation Plant has served as a large-scale pilot plant that has already established the feasibility of reclaiming municipal waste water for ground-water recharge. This 12-mgd plant produces clear, safe water, which is spread over the Los Angeles County Flood Control District's flood-water spreading grounds along the San Gabriel and Rio Hondo Rivers and thereby replenishes ground water used by the Los Angeles Metropolitan Water District. The Central and West Basin Water Replenishment Districts pay $12.75 per acre-foot for this renovated water, the same as is paid for imported Colorado River water.

The construction and operation of this treatment plant represents a particularly significant step forward in the water renovation field; first, because this is the first large-scale plant to be built solely for producing re-usable water from a domestic waste stream, and second, because the renovated water is used deliberately to augment a municipal water supply. One of the problems that had to be solved in getting the Whittier Narrows Plant into successful operation involved a highly toxic pollutant, hexavalent chromium, which, present in the raw waste and unremoved by the scheduled treatment processes, exceeded allowable concentration in the effluent stream. The removal problem was solved by isolating the industrial sources contributing this material and making arrangements to divert or treat these products separately to keep them out of the raw waste stream.

The waste waters destined for the spreading grounds are given conventional primary and secondary treatment involving activated sludge. The "advanced treatment" includes chlorination, and since March 1963, foam separation. This latter process reduces the concentration of ABS detergents to less than 2 ppm in the final plant effluent and thereby meets the detergent criterion of the Regional Water Pollution Control Board. Although the plant effluent is of high chemical quality, it is still not suitable for direct municipal use, and further treatment is achieved during percolation through the soil. A detailed test program has shown this latter step to provide (1) additional oxidation of organic compounds after suitable biological growths have accumulated, and (2) conversion of ammonia to nitrates upon development of appropriate nitrifying cultures. Before its re-use, the quality of the renovated water is further improved through dilution with natural ground waters.

Continuous monitoring of the aquifer receiving the reclaimed waste water has been carried out by analyzing samples from a series of wells scattered throughout the Whittier Narrows region. Results to date have shown no evidence that the water quality in the region has been adversely affected through the spreading of this effluent. None of the wells have yet shown evidence of synthetic detergents' being present.

Based on the complete acceptance and success of this plant, the Los Angeles County Sanitation Districts, in their report "A Plan for Water Re-use," has recommended expansion of the water reclamation program in Los Angeles County at a cost of $20 million for eight additional plants to reclaim 100 mgd, approximately one-third of the District's sewered waste waters.

Not all waste streams will be acceptable for recharging ground water supplies after only minimal treatment. Among factors affecting their suitability for this purpose is the concentration of total dissolved solids in both the renovated water and the receiving ground-water supply. Typical of many ground waters today are those of Montebello forebay (Los Angeles area), where total dissolved solids increased from 246 ppm in 1908 to 514 ppm in 1959. Similarly, the concentration of total dissolved solids in waste streams is generally increasing. This established trend serves as a warning that if total dissolved solids in domestic water supplies produced from either of these sources are to be held below the presently recommended 500 ppm limit future waste treatment processes will eventually require inclusion of techniques capable of removing these dissolved materials.

STREAM POLLUTION CONTROL

San Ramon Village, California

Enforcement of stream pollution legislation in recent years has been instrumental in encouraging many communities throughout the nation to construct conventional sewage treatment plants and to discontinue the practice of discharging raw waste waters into natural waterways. Since effluent from secondary treatment plants represents a drastic improvement in quality over raw sewage, these treated effluents have generally been considered acceptable for discharge into surface streams even though some of the original pollutants may remain comparatively unchanged. Nevertheless, the need for additional treatment to remove certain of these "refractory" contaminants is becoming more and more obvious, particularly as stricter standards come into being.

Typical of this trend is the problem presently facing San Ramon Village, California, a rapidly growing community of 1,600 homes, 20 miles east of Oakland, California. The town's domestic wastes receive conventional treatment involving activated sludge. Secondary effluent is chlorinated and discharged into Alameda Creek, which contributes water to the city of San Francisco's nearby percolation beds and thereby indirectly supplies part of the water used by the city of Oakland. The San Francisco Bay Regional Water Pollution Control Board has recently established a limit of 1 ppm ABS for effluents discharged into Alameda Creek. As a result of this ruling, San Ramon Village is obliged to reduce the concentration of ABS in its treatment plant effluent from 4 to 1 ppm.

Faced with the problem of removing a pollutant for which there are only limited laboratory test data concerning effective removal techniques, the managing engineer for the local sewage treatment plant undertook an experimental study to work out a tertiary foaming process capable of effecting the necessary ABS reduction. The approach followed was patterned after the California Research Corporation's experimental process involving foam fractionation and recycle of the collected foam back to the aeration basins. Effectiveness of the proposed recycle method is based on experimental evidence, which has demonstrated that longer exposure of ABS to biological activity will bring about increased degradation. The San Ramon installation represents the first large-scale test of this process.

Lake Tahoe

The situation existing at Lake Tahoe, located in the Sierra Nevada Mountains on the California-Nevada State line is indicative of the intensity of concern that often develops over the disposition of waste waters regardless of the degree of treatment provided. Concern over the possible despoiling of this picturesque lake by inflow or infiltration of sewage treatment plant effluent presently disposed by ground spreading has resulted in considerable effort's being spent to establish the most suitable method of waste disposal for the expanding resort areas and at the same time maintain the water quality necessary to protect the lake as a natural scenic wonder and a national resource.

After a detailed survey of the area and a thorough analysis of the problem, a Board of Consultants selected three possible approaches as satisfactory alternatives to replace the existing practice wherein effluent from primary and secondary treatment processes is spread on the soil in the Lake Tahoe Basin. These were (1) disposal to the lake after "advanced" treatment, (2) export from the Basin, and (3) discharge to the Truckee River after a relatively high degree of treatment.

Since waste effluents applied to the soils in the Basin eventually return to the lake by runoff or percolation, the Board of Consultants pointed out that continuation of this practice could eventually damage the water quality of the lake by introducing additional nitrogen and phosphate nutrients that would promote growth of algae in the now-clear lake waters. They recommended for first consideration discharge of the renovated wastes to the Truckee River after conventional and "advanced treatment" to a degree adequate to produce drinking water. The tertiary treatment considered necessary, and finally adopted, included alum coagulation and filtration followed by chlorination and adsorption on activated charcoal--by far the most elaborate tertiary treatment yet proposed for treating domestic sewage as a water pollution control measure.

The Federal Water Pollution Control Advisory Board recently conducted public hearings inquiring into all aspects of the Lake Tahoe problem with the aim of making recommendations for a satisfactory disposal method. Despite the high degree of treatment proposed by the Board of Consultants, there was almost universal objection by those appearing at the hearing to disposal either in Lake Tahoe or in the Truckee River. Exporting the waste water, after treatment, from the Basin appears to be the only approach that will satisfy all the varied interests concerned. This procedure has been adopted, and the reclaimed water will be used for irrigation in Nevada.

SUMMARY

The foregoing is not intended to be a complete documentation of the extent to which waste waters are presently being re-used or "advanced" waste treatment applied. There are many other examples of re-use in the United States and in other parts of the world, particularly in Israel, where waste-water renovation and re-use play a major role in that nation's overall water management plans. The examples reported here do, however, serve to point out that waste waters are already being re-used in a wide variety of beneficial applications and that the re-use possible is entirely dependent on the level of treatment provided.

While it is true that considerable stream pollution occurs in some areas because the local waste treatment is not maintained even at the level of present conventional technology, it must be accepted that this is an inconsistency resulting from the localized nature of waste-water treatment and stream pollution problems. By the same token, there are other local areas where the highest level of conventional treatment is in use, and where more advanced treatment methods will be employed as soon as they have been developed to the point of technical and economic practicability. As demonstrated by the situation in the Lake Tahoe resort area, the need for highly efficient advanced treatment methods is extremely urgent under extraordinary circumstances such as these, and cost of treatment becomes of secondary consideration if the need is great enough.

APPENDIX B

Name	Period		Funds Committed in FY, $				Area of work
	From	To	1961	1962	1963	1964	
Purchase orders:							
Louis Koenig Research	Nov. '61			2, 360			Injection to underground formations
Louis Koenig Research	Nov. '61	Jan. '62		2, 200			Placement in underground cavities and spreading
D. F. Othmer	March '61	June '61	1, 000				Distillation and evaporation
Richard D. Pomeroy	Nov. '62	Jan. '63			2, 500		AWT parameters
Contracts:							
Aerojet-General	June '63	Nov. '64			41, 515	5, 812	Reverse osmosis
American Machine & Foundry	June '63	May '64			52, 079		Flash evaporation
App. Science Labs., Inc. . . .	June '61	Nov. '61	9, 750				Freezing
W. L. Badger Assoc., Inc. . .	Oct. '62	July '63			13, 372	400	Distillation
U. S. Bureau of Mines	Dec. '62	Dec. '63			17, 000	21, 200	Adsorption of coals
California State Dept. of Health	March '64	March '65				14, 384	Determine consumer attitudes toward mineralized water supplies

APPENDIX B

SUMMARY OF AWTR CONTRACTS THROUGH JUNE 30, 1964

Name	Period		Funds Committed in FY, $				Area of work
	From	To	1961	1962	1963	1964	
Purchase orders:							
W. L. Badger Assoc., Inc.	March '61	April '61	2, 500				Discussion of various processes for removal of soluble materials from waste water
A. J. Barduhn	Feb. '61	June '61	2, 000				Freezing and hydration distillation
Clemson College	Sept. '61	May '64			2, 400		Literature search
J. A. Gerster	March '61	April '61	750				Distillation
K. C. Hickman	March '61	May '61	2, 500				Distillation and other processes
Karl Kammermeyer	June '61	Dec. '62	500				German literature search
Karl Kammermeyer	Jan. '63	Dec. '64			500		German literature search
Louis Koenig Research	Aug. '60	June '61	2, 380				Technical spec. for AWT processes, series of reports
Louis Koenig Research	Nov. '61			2, 200			Incineration

Name	Period		Funds Committed in FY, $				Area of work
	From	To	1961	1962	1963	1964	
Contracts:							
Ionac Chemical Corp.	Nov. '61	Dec. '62		20, 253	3, 000		Coagulation, adsorption, and sludge blanket filtration
Ionics, Inc.	June '61	July '63	2, 000	53, 920	38, 126		Electrodialysis and ion exchange
Ionics, Inc.	June '64	Dec. '64				39, 620	Design and construct electrodialysis pilot plant
Louis Koenig Research	June '61	July '61	2, 490				Oxidation
Louis Koenig Research	March '63	June '64			20, 900		Ultimate disposal
Louis Koenig Research	Nov. '63	Oct. '64				13, 281	Market projection
Los Angeles Co. San. Dists. .	June '63	Sept. '64			63, 500		Recreational reuse, foaming and cost quality
D. F. Othmer	July '61	Oct. '61		2, 250			Extraction
Pennsalt Chemical Co.	May '62	June '63		35, 780	5, 060		Electrochemical degradation
Pittsburgh Chemical Co. . . .	Sept. '61	April '63		69, 426			Adsorption

Name	Period		Funds Committed in FY, $				Area of work
	From	To	1961	1962	1963	1964	
Contracts:							
Carrier Corporation.	Feb. '63	Aug. '63			13, 294		Freezing
Chemical Separation Corp.. .	April '63	April '64			18, 363		Ion exchange regenerant recovery
Dorr Oliver, Inc.	July '63	July '64				44, 768	Feasibility of powdered activated carbon
Dow Chemical	Feb. '63	Feb. '64			22, 170		Evaluation of carbon analyzer
Dow Industrial Service	Dec. '60	Feb. '62	21, 247				Evaluation of use of activated carbons and chemical regeneration in treatment of secondary sewage plant effluents
Esso Research & Eng. Co. . .	Oct. '61	Aug. '62		49, 820			Foaming and foaming-adsorption
General Electric Co.	June '64	Dec. '64				16, 087	Corona discharge
President & Fellows of Harvard College . . .	May '61	Aug. '64	22, 152	23, 699	38, 468		Adsorption
Infilco, Inc.	June '63	Aug. '64			29, 120		Coagulation-filtration

Name	Period		Funds Committed in FY, $				Area of Work
	From	To	1961	1962	1963	1964	
Contracts:							
Pittsburgh Chemical Co. . . .	June '63	June '64			40,471		Adsorption
Polytechnic Inst. of . . . . . . Brooklyn	March '61	Nov. '62	25,510				Electrodialysis and ion exchange
Radiation Applications, Inc. .	April '61	March '64	34,940	45,350	27,889		Foaming
Syracuse University Res. Ins.	Oct. '62	Feb. '64			32,040	5,550	Eutectic freezing
Texas A & M	July '62	July '64			22,174	25,498	Solvent extraction
University of California . . .	June '63	Sept. '64			19,646		Foam separation
TOTAL			129,719	307,258	523,587	186,600	

APPENDIX C

APPENDIX C
LIST OF PUBLICATIONS AND PRESENTATIONS BY AWTR CONTRACTORS REPORTING ON AWTR PROJECTS

Publications

DOW CHEMICAL COMPANY — Contract No. SAph 76290 - Introductory remarks made at panel Symposium on Water Renovation & Desalination programs by Clayton E. Van Hall, recorded in Chemical Engineering Progress Symposium Series, Vol. 59, No. 45, 1963.

ESSO RESEARCH & ENGINEERING COMPANY — Contract No. PH 86-62-26 - Separation of Surface Active Compounds by Foam Fractionation, by Dr. R. M. Skomoroski, published in Journal of Chemical Education, Vol. 40, No. 9, pp. 470-471, 1963.

HARVARD UNIVERSITY — Contract No. SAph 76295 - Kinetics of Adsorption on Carbon From Solution, by Walter J. Weber, Jr., and J. Carrell Morris. Journal of Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers, April 1963.

Removal of Biologically-Resistant Pollutants from Waste Waters by Adsorption by J. Carrell Morris and Walter J. Weber, Jr. Proceedings of International Conference Advances in Water Pollution Research, Vol. 2, p. 231, 1964, MacMillan Co., N. Y.

Determination of Alkyl Benzene Sulfonates by Ultraviolet Spectrophotometry, by Walter J. Weber, Jr., J. Carrell Morris, and Werner Stumm, Analytical Chemistry, Dec. 1962.

Adsorption in Heterogeneous Aqueous Systems, by Walter J. Weber, Jr. and J. Carrell Morris. Journal American Water Works Assn., April 1964.

Determination of Carbon in Waste Waters by High-Temperature Wet Oxidation by Walter J. Weber, Journal of Water Pollution Control Federation, May 1964.

PITTSBURGH CHEMICAL COMPANY — Contract No. PH 86-62-15 - Papers given at ASC Meetings in September 1962 and in Cincinnati, January 1963 by R. S. Joyce. Removal of Organic Compounds from Secondary Sewage Effluent Using Granular Regenerable Activated Carbon, R. S. Joyce, Submitted to Water Pollution Control Federation Journal.

ROCHESTER INSTITUTE OF TECHNOLOGY — Purchase Order 2659 - Role of Distillation in a Waste Water Recovery Cycle, by Kenneth C. D. Hickman. Journal American Water Works Assn., September 1963.

DOW CHEMICAL COMPANY — Contract No. SAph 76290 - Introductory remarks made at panel Symposium on Water Renovation & Desalination programs, recorded in Chemical Engineering Progress Symposium Series, Vol. 59, No. 45, 1963.

ESSO RESEARCH & ENGINEERING COMPANY — Contract No. PH 86-62-26 - Renovation of Waste Water by Foam Fractionation, by Drs. Skomoroski and Eldib. Paper presented at the ACS Meeting of Jan. 1963 in Cincinnati to the Division of Water & Waste Chemistry.

Renovation of Waste Water Effluents by Foam and Emulsion Fractionation, by Dr. I. A. Eldib. Presented at the Gordon Research Conference on Separations and Purifications in August 1962.

HARVARD UNIVERSITY — Contract No. SAph 76295 - Removal of Biologically-Resistant Pollutants from Waste Waters by Adsorption by J. Carrell Morris and Walter J. Weber, Jr., presented by J. Carrell Morris at International Conference on Water Pollution Research, London, England, Sept. 3-7, 1962.

A Physical Chemist's View of Water Renovation, by J. Carrell Morris. Presented at A. I. Ch. E. Meeting, San Juan, Puerto Rico, Sept. 29-Oct. 3, 1963.

Kinetics of Adsorption in Columns of Fluidized Media by Walter J. Weber. Presented at WPCF Meeting in Seattle, Oct. 1963.

IONICS, INC. — Contract No. SAph 76690 - The Removal of ABS and Other Refractories from Water by Electrodialysis and Associated Means by C. Berger and H. L. Chew. Presented at the USPHS Seminar on Advanced Waste Treatment Research, Cincinnati, Ohio, May 15, 1962.

Use of Electrodialysis for Removal of Inorganic Refractories from Waste Water, by J. D. Smith, H. L. Chew, and J. L.

Eisenmann. Paper presented at ACS Symposium on Waste Water Renovation, Cincinnati, Ohio, Jan. 14-16, 1963.

Electrodialysis in Waste Water Recycle by J. D. Smith and J. L. Eisenmann, presented at Industrial Waste Conference held at Purdue University, May 1964.

Presentations

PITTSBURGH CHEMICAL COMPANY — Contract No. PH 86-62-15 - R. S. Joyce gave papers at ACS Meeting in September 1962 and in Cincinnati, Jan. 1963.

AEROJET-GENERAL CORP. — Contract No. PH 86-63-227 - Waste Water Renovation by Reverse Osmosis, by B. Keilin and L. M. Tint. Presented at A. I. Ch. E. Meeting, Las Vegas, Nevada, Sept. 1964.

BUREAU OF MINES, Pittsburgh Coal Research Center — The Use of Coal and Coal-Derived Materials as Adsorbents for Removing Organic Contaminants from Final Waste Waters, by G. E. Johnson, J. H. Field, and A. J. Forney. Presented at ASC Meeting, Chicago, Sept. 1964.

CARRIER RESEARCH & DEVELOPMENT COMPANY — Contract PH 86-63-59 - Recovery of Usable Water From Waste Water by Freezing, by P. J. Lunde and C. A. Johnson. Presented at A. I. Ch. E. Meeting, Las Vegas, Nevada, Sept. 1964.

DORR OLIVER — Contract No. PH-86-64-5 - Removal of Refractory Organics from Waste Water with Powdered Activated Carbon, by David S. Davies and Robert A. Koplan. Presented at A. I. Ch. E. Meeting, Las Vegas, Nevada, Sept. 1964.

APPENDIX D

APPENDIX D

ADVANCED WASTE TREATMENT RESEARCH PUBLICATIONS

Although over-all guidance of AWTR research projects is provided by the AWTR Program, the results obtained, opinions expressed, and conclusions reached by the contractors are theirs and are not necessarily endorsed by the Department of Health, Education, and Welfare. Except for editorial review and abridgments as necessary, these reports appear as received from the contractors.

		Report Number
AWTR-1	Summary Report, June 1960 - December 1961	W62-9
AWTR-2	Preliminary Appraisal of Advanced Waste Treatment Processes	W62-24
AWTR-3	Ultimate Disposal of Advanced Treatment Waste	999-WP-3
	Part 1. Wet Oxidation	
	Part 2. Incineration	
AWTR-4	Waste-Water Renovation	999-WP-4
	Part 1. A Design Study of Freezing and Gas Hydrate Formation	
	Part 2. Feasibility Tests of Freezing	
AWTR-5	Contaminant Removal from Sewage Plant Effluents by Foaming	999-WP-5
AWTR-6	Cost of Purifying Municipal Waste Waters by Distillation	999-WP-6
AWTR-7	Advanced Waste Treatment by Distillation	999-WP-9

		Report Number
AWTR-8	Ultimate Disposal of Advanced-Treatment Waste	999-WP-10
	Part 1. Injection	
	Part 2. Placement in Underground Cavities	
	Part 3. Spreading	
AWTR- 9	Adsorption of Biochemically Resistant Materials from Solution 1.	999-WP-11
AWTR-10	Feasibility of Granular, Activated-Carbon Adsorption for Waste-Water Renovation	999-WP-12
AWTR-11	Evaluation of the Use of Activated Carbon and Chemical Regenerants in Treatment of Waste Water	999-WP-13
AWTR-12	Evaluation of Various Adsorbents and Coagulants for Waste-Water Renovation	999-WP-14
AWTR-13	Electrochemical Treatment of Municipal Waste Water	999-WP-19
AWTR-14	Summary Report: The Advanced Waste Treatment Research Program. January 1962 through June 1964	999-WP-24